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Amorphous tetrafluoroethylene-hexafluoropropylene copolymers

Abstract:

Disclosed herein are novel amorphous tetrafluoroethylene-hexafluoropropylene (TFE-HFP) copolymers, which are more random than previous amorphous TFE-HFP copolymers, as well as a novel high productivity continuous process for making these polymers. The polymers are particularly useful in the form of coatings, films and encapsulants.

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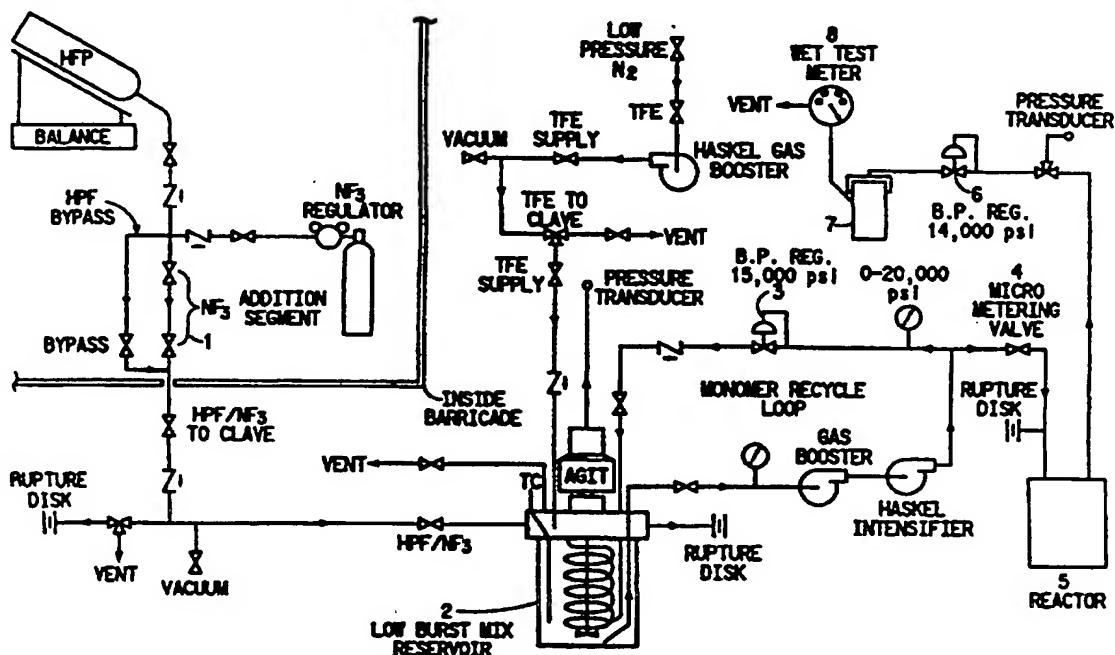
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(54) Title: AMORPHOUS TETRAFLUOROETHYLENE-HEXAFLUOROPROPYLENE COPOLYMERS



(57) Abstract

Disclosed herein are novel amorphous tetrafluoroethylene-hexafluoropropylene (TFE-HFP) dipolymers, and other copolymers containing TFE, HFP and a third monomer, many of which are more random than previous amorphous TFE-HFP copolymers, as well as a novel high productivity continuous process for making these polymers. The polymers are particularly useful in the form of coatings, films and encapsulants.

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TITLE**AMORPHOUS TETRAFLUOROETHYLENE-
HEXAFLUOROPROPYLENE COPOLYMERS****FIELD OF THE INVENTION**

5 This invention concerns copolymers containing hexafluoropropylene and tetrafluoroethylene which are amorphous. They may be produced by a novel high pressure continuous process.

TECHNICAL BACKGROUND

10 Amorphous fluorinated polymers, particularly perfluorinated polymers, are highly useful, particularly as coatings and encapsulants, because of their unusual surface properties, low refractive index, low dielectric constant., and the relative ease of coating or encapsulating objects with such polymers. However, the use of such polymers has been limited because of their high cost, which usually derives from the high cost of the monomers and/or the high cost of the polymerization
15 process to make the polymers. Therefore, such polymers, and the processes for making them, which are lower in cost are constantly being sought.

 U.S. Patent 3,062,793 describes amorphous copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) which are made by a high pressure free radical polymerization. The only process described therein is a batch process
20 which has a relatively low productivity.

SUMMARY OF THE INVENTION

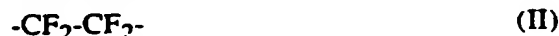
 This invention concerns a continuous polymerization process, comprising, contacting at a pressure of about 41 MPa to about 690 MPa, and a temperature above about 200°C, preferably about 200°C to about 400°C, tetrafluoroethylene,
25 hexafluoropropylene, and a radical initiator, to produce an amorphous polymer which contains at least 30 mole percent, of repeat units derived from said hexafluoropropylene, at least 1 mole percent of repeat units derived from said tetrafluoroethylene, and provided that said continuous polymerization has an average residence time of about 5 seconds to about 30 minutes.

30 This invention also concerns an amorphous polymer, consisting essentially of repeat units of the formula:

(a) at least about 30 mole percent of



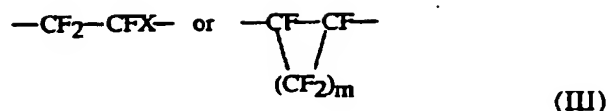
(b) at least about 1 mole percent



35

and

(c) 0 to about 10 mole percent



5 wherein X is $-\text{C}_n\text{F}_{2n+1}$ or $-\text{OC}_n\text{F}_{2n+1}$, m is 2, 3 or 4, and n is either an integer of 2 to 20 with alkyl groups $-\text{C}_n\text{F}_{2n+1}$ or an integer of 1-20 with alkoxy groups $-\text{OC}_n\text{F}_{2n+1}$.

provided that in said polymer less than 20 mole percent of (I) is present in the form of triads.

10 The invention also concerns a continuous polymerization process, comprising, contacting at a pressure of about 41 MPa to about 690 MPa, and a temperature of about 200°C to about 400°C, tetrafluoroethylene, hexafluoropropylene, and a third monomer and a radical initiator, to produce an amorphous polymer which contains at least 15 mole percent, preferably 30 mole percent of repeat units derived from said hexafluoropropylene, at least 0-70 mole percent of repeat units derived from said tetrafluoroethylene, and 0-70 mole percent of repeat units derived from said third monomer, and provided that said continuous polymerization has an average residence time of about 5 seconds to about 30 minutes.

20 This invention also concerns a compound of the formula $(\text{C}_4\text{F}_9)_2\text{NSCF}_3$. A novel compound herein is $\text{R}^6\text{R}^7\text{CFSO}_2\text{R}^8$ wherein R^6 is perfluoroalkyl, perfluoroalkyl containing one or more ether oxygen atoms, perfluoroalkoxy or perfluoroalkoxy containing one or more ether oxygen atoms, R^7 is perfluoroalkyl or perfluoroalkyl containing one or more ether oxygen atoms, and R^8 is perfluoroalkyl. It is preferred that each of R^6 , R^7 and R^8 independently contain 1 to 30 carbon atoms. It is also preferred that R^8 is perfluoro-n-alkyl containing 1 to 20 carbon atoms. It is more preferred that R^6 is perfluoro-n-propoxy, R^7 is trifluoromethyl, and R^8 is perfluoro-n-octyl. This compound is useful as an initiator for the polymerizations described herein.

30 Also disclosed herein is an amorphous polymer containing repeat units derived from:

27-60 mole percent hexafluoropropylene, up to 35 mole percent total of one or more second monomers, and the balance tetrafluoroethylene, provided that at least one mole percent of TFE is present in the polymer, and wherein said second monomer is ethylene, vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene, 2,3,3,3-tetrafluoropropene, 4-bromo-3,3,4-tetrafluoro-1-butene, $\text{CH}_2=\text{CHO}(\text{C}=\text{O})\text{R}^2$ wherein R^2 is perfluoro-n-alkyl containing 1 to 8 carbon

atoms, $\text{CH}_2=\text{CHR}^3$ wherein R^3 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OR}^4$ wherein R^4 is $\text{C}_n\text{F}_x\text{H}_y$ wherein $x+y = 2n+1$ and n is 1 to 8, chlorotrifluoroethylene, or allyltrimethoxysilane;

27-60 mole percent hexafluoropropylene, up to 5 mole percent total of one or more fourth monomers and the balance tetrafluoroethylene, provided that the polymer contains at least 1 mole percent tetrafluoroethylene, wherein said fourth monomer is perfluorocyclopentene, perfluorocyclobutene, $\text{CF}_2=\text{CFCF}_2\text{CN}$, $\text{CF}_2=\text{CFR}^5$ wherein R^5 is perfluoroalkyl optionally containing one or more of one or more ether groups, one cyano group, or one sulfonyl fluoride group, perfluoro-(2-methylene-4-methyl-1,3-dioxolane), perfluoro(2-methyl-2,3-dihydro-1,4-dioxin), or $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$; or

up to 30 mole percent total of one or more second monomers and up to 5 mole percent total of one or more fourth monomers.

Described herein is an amorphous copolymer, consisting essentially of:

- (a) >15 mole percent of the repeat unit
 $-\text{CF}(\text{CF}_3)-\text{CF}_2-$ (I)
- (b) at least 1 to about 60 mole percent of the repeat unit
 $-\text{CF}_2-\text{CF}_2-$ (II)
- (c) about 0.1 to about 85 mole percent of the repeat unit
 $-\text{CH}_2-\text{CF}_2-$ (IV)
- wherein no more than about 20 mole percent of (I) is present in triads.

Also described herein is an amorphous copolymer, consisting essentially of repeat units of the formula:

- (a) >15 mole percent of the repeat unit
 $-\text{CF}(\text{CF}_3)-\text{CF}_2-$ (I)
- (c) about 0.1 to about 85 mole percent of the repeat unit
 $-\text{CH}_2-\text{CF}_2-$ (IV)
- wherein no more than about 20 mole percent of (I) is present in triads.

DETAILS OF THE INVENTION

The TFE/HFP copolymer made herein is amorphous. By an amorphous polymer is meant that the polymer has a heat of melting of less than 1 J/g when measured by Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min, in the case of a TFE/HFP dipolymer. This is measured on a "first heat", that is virgin polymer is heated to at least 300°C in the DSC (at 10°C/min), and the heat of melting, if any, is measured. In the case of terpolymers, where the residual third monomer is often removed from the polymer by heating for about four hours,

at 150°C, in a vacuum oven, DSC "second heats", at 10°C/min to at least 200°C, were used.

These polymers are made via a continuous polymerization process in which the initial ingredients are fed to the reactor in an essentially continuous manner and in which the product stream is essentially continuously withdrawn at approximately the same rate at which the ingredients are added. Such types of reactions are generally known to the artisan, see for instance H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., vol. 19, John Wiley & Sons, New York, 1982, p. 880-914. Such continuous reactors include continuous stirred tank reactors and pipeline (tubular) reactors. Under the conditions employed in the process as described herein, the productivity of the process is exceptionally high. By productivity herein is meant the weight of polymer produced in a unit volume of reactor in a unit volume of time. Productivities herein are reported as kg/L/hr.

The process described herein has typical productivities of about 0.8 to about 15 kg/L/hr. The Examples illustrate that typically higher polymerization temperatures give higher productivities. By contrast, a batch polymerization, making a somewhat similar polymer, reported in U.S. Patent 3,062,793, has productivities (from the Examples) of about 0.01 to about 0.03 kg/L/hr, more than an order of magnitude less than that for the continuous process. This means a lower cost for polymer produced by the continuous process.

The process is run at a pressure of about 41 to about 690 MPa (~6,000 to ~100,000 psi), preferably about 55 to about 172 MPa (~8,000 to ~25,000 psi), more preferably about 62 to about 152 MPa (~9,000 to about 22,000 psi), and especially preferably about 69 to about 103 MPa (~10,000 to ~15,000 psi). As pressure drops down towards 41 MPa the molecular weight of the polymers formed and the conversion of monomers to polymer both tend to drop.

It is preferred that solvents not be used in the process, since at these pressures the monomers, particularly HFP, usually dissolve the polymer. Nonetheless, solvents can be used in the reactor. If the final product is to be a polymer solution, making the polymer solution directly may be preferable, to reduce costs (see Example 43). Sometimes for convenience in handling, small quantities of initiator are best introduced when diluted to a larger volume with a small amount of solvent (see Example 51). Solvent may also be used for other reasons, such as to decrease the viscosity of the process mixture, or to help keep lines clear of polymer, particularly at lower pressures. When solvents are used it is preferred that they be essentially inert under process conditions. Useful solvents include perfluorodimethylcyclobutane and perfluoro(n-butyltetrahydrofuran).

The polymer is soluble in the monomer(s) under the process conditions. Therefore, one method of polymer isolation is to reduce the pressure below that required for solution of the polymer, and isolate the polymer from that, as by decantation, filtration or centrifugation. Indeed, it may not be necessary to reduce
 5 the pressure of the unreacted monomers to atmospheric pressure, but merely that required for phase separation of the polymer. Therefore these monomers can be recycled with only a "partial" repressurization, thereby saving energy costs. Alternatively the pressure can be reduced to atmospheric pressure, while the volatile monomers are vented off, leaving the product polymer. The monomers
 10 can of course be recovered and reused.

The apparatus for running the polymerization may be any suitable pressure apparatus in which the reactant and products streams may be added and removed at appropriate rates. Thus the apparatus may be a stirred or unstirred autoclave, a pipeline type reactor, or other suitable apparatus. Agitation is not necessary, but
 15 preferable, especially to obtain polymers with low MWD's. The material of construction should be suitable for the process ingredients, and metals such as stainless steel are often suitable.

The polymerization is carried out above about 200°C, preferably from about 200 to about 400°C, more preferably from about 225 to about 400°C, and
 20 most preferably from about 250 to about 400°C. The initiator is chosen so that it will generate active free radicals at the temperature at which the polymerization is carried out. Such free radical sources, particularly those suitable for hydrocarbon vinyl monomers at much lower temperatures, are known to the artisan, see for instance J. Brandrup, et al., Ed., Polymer Handbook, 3rd Ed., John Wiley & Sons,
 25 New York, 1989, p. II/1 to II/65. The preferred temperature for running our process depends on both the monomers and the initiator and is often a compromise between raising temperature to favor high productivities and high conversions and lowering temperature to minimize chain transfer and monomer degradation. For the copolymerization of HFP with TFE, for example, where chain transfer is not a
 30 problem, $C_2F_5SO_2C_2F_5$ initiation is a good choice on account of the very high productivities it affords at 400°C. For the polymerization of HFP/TFE/PMVE, however, where PMVE chain transfer is of prime concern, NF_3 which retains good efficiency at 250°C, is an excellent choice for initiator.

Suitable free radical initiators include NF_3 , R_fNF_2 , $R_{f2}NF$, $R_{f3}N$,
 35 $R^1N=NR^1$, R_fOOR_f , perfluoropiperazine, and hindered perfluorocarbons of the formula C_nF_{2n+2} such as are described in World Patent Application 88/08007, wherein each R_f is independently perfluoroalkyl, preferably containing 1 to 20 carbon atoms, hindered perfluoroalkenes of the formula C_nF_{2n} , perfluoro-

(dialkylsulfones) of the formula $R^1SO_2R^1$, perfluoroalkyl iodides of the formula R^1I , R^1SO_2F , R^1SO_2Cl , $ClSO_2Cl$, perfluoroalkylene diiodides of the formula IR^6I where the two iodides are not vicinal or geminal wherein R^6 is perfluoroalkylene containing 3 to 20 carbon atoms, perfluoro(dialkyldisulfides) R^1SSR^1 , and

5 perfluoroalkyl compounds containing nitrogen-sulfur bonds of the formula $R^1_2NSR^1$, wherein each R^1 is independently saturated perfluorohydrocarbyl optionally containing one or more ether groups, isolated iodine, bromine or chlorine substituents, or perfluoroamino groups. By "saturated perfluorohydro-

10 unsaturated carbon-carbon bonds. By an "isolated" iodine, bromine or chlorine substituent is meant that there are no other iodine, chlorine or bromine atoms on carbon atoms alpha or beta to the carbon atom bonded to the isolated iodine, bromine or chlorine atom. All of these initiators are illustrated in one or more of the Examples. Some of these initiators may only be active at the higher end of the

15 temperature range of the polymerization process. This too is illustrated in the Examples, and the activity of any particular initiator molecule may be readily determined by minimal experimentation. Preferred initiators are NF_3 , R_2NF , R_3NF_2 , perfluoropiperazine, perfluoro(dialkylsulfones), i.e. $R^1SO_2R^1$, and hindered perfluorocarbons. NF_3 is an especially preferred initiator. If higher

20 molecular weight polymers are desired, the initiator should preferably not have any groups present in its structure that cause any substantial chain transfer or termination during the polymerization. Such groups usually include, for instance, organic bromides or iodides or carbon-hydrogen bonds.

The amount of free radical initiator used will vary depending on process

25 conditions. Generally speaking an effective amount is used, an effective amount being that which causes more polymerization to take place with the initiator than without. It is likely that any polymerization without deliberately added initiator present is due to adventitious impurities which can act as initiators at the high polymerization temperatures. Effort should be made to minimize these impurities,

30 such as oxygen. A useful range of initiator concentration has been found to be about 0.003 to about 0.5 g of initiator/kg monomer, preferably about 0.1 to about 0.3 g/kg. Higher or lower amounts are also useful depending upon the initiator, the monomers, goal molecular weights, process equipment, and process conditions used, and can readily be determined by experimentation. The initiator may be

35 added to the reactor as a solution in the monomer(s).

While "solvents" may be added to the polymerization so that the polymerization is carried out in solution or slurry, it is preferred if little or no solvent is added. The polymer formed is often soluble in the supercritical HFP

under the process conditions. The polymer may be isolated simply by reducing the pressure below about 34 MPa (~5,000 psi), at which point the polymer becomes insoluble. The polymer may also be isolated as fibers or fibrils by flash spinning from solvent and by direct flash spinning of the polymerization mixture. Small amounts of solvents may be used for convenience, as for a carrier for the initiator. FC-75, perfluoro(2-n-butyltetrahydrofuran), and the cyclic dimer of HFP are examples of useful solvents. Another useful solvent is supercritical CO₂.

The polymer produced by the instant process is amorphous. Whether this type of a polymer would be amorphous depends on the composition (relative amounts of HFP and TFE and other monomers if present), and the distribution of the two repeat units in the polymer. If a dipolymer, the polymer product should preferably contain at least about 30 mole percent of (I) and at least 1 mole percent of (II), preferably at least 30 mole percent of (II), more preferably about 35 to about 50 mole percent of (I) and about 50 to about 65 mole percent of (II) when a dipolymer is made [no repeat unit (III) present]. Optionally up to about 10 mole percent of repeat unit (III) may be present. When (III) is present a preferred composition is about 35 to about 65 mole percent (I), about 35 to about 65 mole percent (II), and about 0.1 to about 10 mole percent of (III). Various comonomers (III) may be used in the polymerization process, and be incorporated into the polymer. Perfluoro(alkyl vinyl ethers) and perfluorinated terminal alkenes, each optionally substituted with ether, cyano, halo (other than fluorine), sulfonyl halide, hydrogen or ester groups may be used. Also unfluorinated or partially fluorinated olefins or vinyl ethers, optionally substituted as above, may also be used. Useful comonomers include CF₂=CFOCF₂CF(CF₃)OCF₂CF₂SO₂F, ethylene, propylene, isobutylene, vinylidene fluoride, vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene, 2,3,3,3-tetrafluoropropene, 4-bromo-3,3,4,4-tetrafluoro-1-butene, perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene), CF₂=CF(CF₃)COF, CH₂=CHO(C=O)R² wherein R² is perfluoro-n-alkyl containing 1 to 8 carbon atoms, CH₂=CHR³ wherein R³ is perfluoro-n-alkyl containing 1 to 8 carbon atoms, CH₂=CH(C=O)R⁴ wherein R⁴ is C_nF_xH_y wherein x+y = 2n+1 and n is 1 to 8, allyltrimethoxysilane, perfluorocyclopentene, perfluorocyclobutene, CF₂=CFCF₂CN, CF₂=CFR⁵ wherein R⁵ is perfluoroalkyl optionally containing one or more of one or more ether groups, cyano groups, and/or sulfonyl fluoride groups and preferably only one cyano or sulfonyl fluoride is present, perfluoro(2-methylene-4-methyl-1,3-dioxolane), perfluoro(2-methyl-2,3-dihydro-1,4-dioxin), FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, methyl vinyl ether, CFCI=CF₂, CH₂=CFCF₃, CH₂=CHCF₃, CH₂=CHCF₂CF₂CF₂CF₃, CH₂=CHCF₂CF₂Br, CF₂=CFCF₂CN, and CF₂=CFCF₂OCF₂CF₂SO₂F. In

preferred compounds R^2 is trifluoromethyl, R^3 is trifluoromethyl or perfluoro-n-butyl, R^4 is 1,1,1,3,3,3-hexafluoroisopropyl, and R^5 is $-\text{CF}_2\text{CN}$.

The above monomers (and others) can be used to make copolymers containing repeat units derived from HFP, TFE and one or more of the above monomers of the following compositions, and in these compositions:

>30 mole percent HFP, up to 25 mole percent X with the balance TFE, provided the polymer contains at least 1 mole percent TFE, wherein X is ethylene propylene, isobutylene, or methyl vinyl ether;

>15 mole percent HFP, 0.1 to 85 mole percent vinylidene fluoride, and up to 60 mole percent TFE (note that this polymer may also be a dipolymer of HFP and vinylidene fluoride), preferably >20 mole percent HFP, 0.1 to 75 mole percent vinylidene fluoride and up to 60 mole percent TFE, and more preferably >30 mole percent HFP, 0.1 to 65 mole percent vinylidene fluoride and up to 60 mole percent TFE;

>30 mole percent HFP, up to 2 mole percent $\text{CF}_2=\text{CF}(\text{CF}_3)\text{COF}$, with the balance TFE, provided the polymer contains at least 1 mole percent TFE;

27-60 mole percent HFP, up to 35 mole percent X, and the balance TFE provided that at least one mole percent of TFE is present in the polymer, wherein X is vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene, ethylene 2,3,3,3-tetrafluoropropene, 4-bromo-3,3,4,4-tetrafluoro-1-butene, $\text{CH}_2=\text{CHO}(\text{C}=\text{O})\text{R}^2$ wherein R^2 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CHR}^3$ wherein R^3 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OR}^4$ wherein R^4 is $\text{C}_n\text{F}_x\text{H}_y$ wherein $x+y = 2n+1$ and n is 1 to 8, chlorotrifluoroethylene, and allyltrimethoxysilane, and preferred polymers contain 30-50 mole percent HFP, up to 20 mole percent X and the balance TFE, and more preferred polymer contain 30-45 mole percent HFP, up to 10 mole percent X and the balance TFE.

27-60 mole percent HFP, up to 5 mole percent X and the balance TFE provided that the polymer contains at least 1 mole percent TFE, wherein X is perfluorocyclopentene, perfluorocyclobutene, $\text{CF}_2=\text{CFCF}_2\text{CN}$, $\text{CF}_2=\text{CFR}^5$ wherein R^5 is perfluoroalkyl optionally containing one or more of one or more ether groups, one cyano group, or one sulfonyl fluoride group, perfluoro(2-methylene-4-methyl-1,3-dioxolane), perfluoro(2-methyl-2,3-dihydro-1,4-dioxin), or $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, and preferred polymers contain 30-50 mole percent HFP, up to 2 mole percent X and the balance TFE.

In all polymers which contain a monomer other than HFP, TFE and vinylidene fluoride, it is preferred that minimum level of additional monomer is 0.05, more preferably 0.1 mole percent. Also more than one monomer "X" may be

present in any of the above polymers. When the "limitation" on any particular monomer or monomers "X" is a given percentage, the polymer may contain up to that percentage (total) of that "type" of monomer in the polymer. For example a copolymer may contain up to 35 mole percent combined of trifluoroethylene and 3,3,3-trifluoropropene, or another polymer may contain up to 5 mole percent $\text{CF}_2=\text{CFCF}_2\text{CN}$ and up to 30 mole percent 3,3,3-trifluoropropene. The total amount of "X" which may be in the copolymer may not exceed the highest amount for any of the individual monomers, as given above.

Polymer containing HFP, vinylidene fluoride (VF2) and optionally TFE may be analyzed by ^{19}F NMR to determine the microstructure of the polymer. In particular, the microstructure of monomer sequences of isolated repeat units derived from HFP and "surrounded" by monomer units derived from VF2 may be determined. These are:

<u>Sequence ID</u>	<u>Sequence No.</u>	<u>Sequence</u>
$\beta-\beta'(\text{CH}_2)$	1	$\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{CH}_2\text{CF}_2$
$\beta-\gamma(\text{CH}_2)$	2	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{CH}_2$
$\alpha-\gamma-\gamma(\text{CH}_2)$	3	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2$
$\alpha-\beta'(\text{CH}_2)$	4	$\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2$
$\alpha-\gamma(\text{CH}_2);\delta(\text{CF}_3)$	5	$\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)$

Herein the above sequences will be referred to by their Sequence No. For determining these sequences, ^{19}F NMR spectra were acquired on 5% solutions in hexafluorobenzene (HFB). Spectra were taken at 80°C on a Bruker AC 250 operating at 235.4 MHz for ^{19}F . The acquisition conditions included a 90 degree pulse width of 5.0 μsec , 20 second recycle delay, and 64 co-added scans. Spectra were referenced to HFB at -162.46 ppm.

Composition was determined from the ^{19}F NMR spectrum in the following way. Because of the high concentration of HFP, it was assumed that all VF2 next to HFP was represented by the signal at -75 ppm. VF2 which was non-adjacent to HFP was taken from the signal at -82 ppm. The sum of these areas was converted to moles of VF2. The amount of HFP was determined from the sum of the areas at -75 ppm and -70 ppm, converted into moles of HFP. In samples containing TFE, the TFE was determined from the area of the signals between -95 and -125 ppm corrected for CF_2 s from HFP and corrected for the CF_2 s from VF2 represented in the signal of HFP CF_3 s adjacent to CH_2 s from VF2 adjacent to CH_2 s from VF2.

For at least one sample, the composition of VF2 determined in this manner was confirmed by adding an internal standard of trifluoromethyldichlorobenzene to

a weighed amount of polymer and determining the amount of CF_2 from the ^1H spectrum. For the sample tested, the results agreed within 3% relative.

HFP centered sequences were used as a way to identify differences in polymerization. The ^{19}F signal at -179 to -179.5 ppm was identified as the CF in an HFP centered VF2/HFP/VF2 sequence in which the CH_2 's are beta to the CF. The signal at -180.4 to -181.2 ppm was identified as a CF in a VF2/HFP/VF2 sequence in which there were one CH_2 alpha and one CH_2 beta to the CF in the HFP. The final signal at -181 to -181.8 ppm was identified as VF2/HFP/VF2 in which one CH_2 is alpha and one CH_2 is gamma and one CF_3 is delta to the CF.

All of the polymers herein may be crosslinked by methods known in the art. Perfluorinated polymers may be crosslinked by exposure to ionizing radiation. Polymers containing hydrogen or functional groups such as nitrile or sulfonyl halide may be crosslinked by methods known in the art. When crosslinked these polymers are of course crosslinked elastomers if their Tg is below ambient temperature.

As mentioned above, the properties of the polymer will be affected not only by the overall composition of the polymer, but by the distribution of the various monomer units in the polymer. The instant process yields a polymer in which the monomer units are more uniformly distributed in the polymer, which gives polymer with more consistent properties. One measure of polymer uniformity is randomness of the monomer units in the polymer. A measure of this is relative amounts of isolated repeat units, diads, triads etc. By diads and triads are meant instances in which two or three repeat units from the same monomer, respectively, occur in the polymer.

Many of the polymers (including some of the polymers containing 3 or more different repeat units) made by the process described herein have relatively small amounts of triads of repeat unit (I), which of course derived from HFP. Thus in such polymers less than 20 mole percent of (I) is in the form of triads, and preferably less than about 15% and more preferably less than about 10%. As would be expected, in polymers with higher amounts of (I), there is a tendency towards higher triad content. The amount of triads in the polymer can be determined by ^{19}F NMR (see below for procedure). See the summary of triad data for polymers prepared in Examples 23 and 33-36 in the table following Examples 45 to 49. See Examples 23 and 33-36 and Comparative Example 1 for triad amounts in various polymers.

The instant polymers also have a narrower molecular weight distribution (MWD) than prior art polymers. By MWD is meant the weight average molecular weight divided by the number average molecular weight (M_w/M_n). Polymers

described herein often have MWD's of less than 5, preferably less than 4. Such polymers often have a better combination of processability and physical properties.

Repeat unit (III) may be present to help suppress crystallization and/or lower a glass transition temperature, or for other purposes, and are derived from the corresponding α -perfluoroolefin, perfluorocycloolefin or perfluoro(alkyl vinyl ether). Preferred monomers for unit (III) in which $-C_nF_{2n+1}$ is present are those in which $-C_nF_{2n+1}$ is perfluoro-n-alkyl. When X is $-C_nF_{2n+1}$ it is preferred if n is 2 to 14, while if X is $-OC_nF_{2n+1}$ it is preferred if n is 1 to 4, more preferably 1 or 3.

Since TFE is considerably more reactive in the polymerization than HFP, an excess of HFP is needed to achieve the desired polymer composition. Typically this also means that at the end of the polymerization, much or all of the TFE will have polymerized, but there will be (a considerable amount of) unpolymerized HFP. In a sense this is an advantage, since the HFP can act to help carry the polymer from the reactor, and no additional carrier (such as a solvent) is needed. Typically the TFE will be about 1 to 15 mole percent of the total amount of monomer being fed to the process, with the HFP and other monomer(s) (if present) being the remainder.

The average residence time is the average amount of time any of the material fed to the reactor actually spends in the reactor, and is a function of the volume of the reactor and the volumetric flow of the process ingredients through the reactor. A preferred residence time is about 20 sec to about 10 min, more preferably about 30 sec to about 5 min, especially preferably about 40 sec to about 2 min. A minimum preferred residence time is about 10 sec., more preferably about 15 sec.. A maximum preferred residence time is 10 min.

When the process fluids are being added to the reactor, it is preferred if they are preheated just before they enter the reaction to a temperature somewhat less than that of the actual reactor temperature, about 20°C to about 100°C less. This allows one to maintain a uniform constant temperature in the reactor itself, and for the newly added materials to start the polymerization reaction immediately upon entry to the reactor.

The amorphous polymers described herein are useful in a variety applications, many of which are related to the fact that the polymers are readily soluble in certain halogenated, especially perfluorinated solvents. and so the polymers are readily useable as films, coatings and encapsulants. Useful solvents include "dimer", perfluorobenzene, perfluoro(n-butyltetrahydrofuran), and FC-10 (tradename of "dimer" 3M fluorocarbon fluid). Another type of useful solvent is a perfluorinated (organic) compound containing sulfur, such as perfluoro-1,4-

dithiane, perfluorothiepane, perfluorodiethylsulfone, and perfluorooctanesulfonyl fluoride.

In one preferred form, the solvent used to form solutions of the amorphous polymers herein is a mixed solvent. By a mixed solvent is meant a solvent that contains two or more liquid compounds that are miscible with each other in the proportion used. The compounds in the mixed solvent need not be solvents for the amorphous polymer if used alone, but it is preferred that at least one of the compounds of the mixed solvent is a solvent for the amorphous polymer. It is preferred that one of the compounds of the mixed solvent be a perfluorinated compound, as described in the preceding paragraph. Another preferred compound is a hydrofluorocarbon or hydrochlorofluorocarbon as described in Example 128. A preferred procedure for forming a solution of the amorphous polymer in a mixed solvent is to dissolve the amorphous polymer in a perfluorinated compound, and then add the other compound(s).

Since the polymers are relatively chemically resistant, they may be used to encapsulate articles which must be protected from contamination, corrosion and/or unwanted adhesion to other materials. Films and coatings may be particularly useful because of the inherent properties of the polymer, such as, lack of crystallinity (polymer is clear), low surface energy (and hence poor wetting by water or most organic liquids), low dielectric constant, low index of refraction, low coefficient of friction, low adhesion to other materials, etc.

The TFE/HFP copolymers (including di- and terpolymers) of this invention can be used in many ways. One use is as a processing aid in polyolefins. This aspect of the invention is discussed in detail below.

The TFE/HFP and TFE/HFP/(III) copolymer solutions and copolymer/solvent systems of this invention can be used in many ways, making it possible to achieve end results that could not be achieved with previously available perfluoropolymers or could be achieved only in less convenient ways. These results include any of the results for which polymer solutions are used, such as coating, encapsulation, impregnation, and the casting of film. The copolymer solutions and copolymer/solvent systems of the invention can be employed in any of the methods by which solutions are known to be used, including dipping, painting, and spraying.

The copolymer solutions and copolymer/solvent systems of this invention can be used to make coatings on a broad range of substrate materials, including metal, semiconductor, glass, carbon or graphite, and natural and synthetic polymers. The substrates can be in a broad range of physical forms, including film or paper, foil, sheet, slab, coupon, wafer, wire, fiber, filament, cylinder, sphere, and

other geometrical shapes, as well as in a virtually unlimited number of irregular shapes. Coatings can be applied by methods known in the art, including dipping, spraying, and painting. For plane substrates of suitable dimensions, spin coating can be employed. Porous substrates can also be coated or impregnated. These
5 include, for example, screens, foams, microporous membranes, and woven and non-woven fabrics. In making such coatings, the solvent can be driven off by heat leaving a dry copolymer coating. Another advantage is that extremely thin coatings can be achieved, as thin as 100 angstroms or possibly even thinner depending on the coating characteristics required.

10 Coatings of the copolymers of this invention can be a sole coating on a substrate, or a component of a multilayer coating. For example, a TFE/HFP copolymer coating of this invention can be used as a first or primer, intermediate, or final coating in a multilayer fluoropolymer coating system. The coatings of this invention include coatings resulting from several successive applications of solution
15 or copolymer/solvent systems to increase coating thickness to desired levels.

Coatings of this invention can consist of the copolymers of this invention alone, or of the copolymers admixed with minor amounts of other materials either soluble in the solvent or dispersed in the coating solution, suspension, or copolymer/solvent system. A minor amount can be up to about 10 wt% based on
20 the combined weight of copolymer and additive.

Specific coated articles are within the scope of this invention.

Coated articles include polymer extrusion dies and molds for rubber and plastic parts, such as o-rings, bottle caps, golf balls, golf ball covers, golf ball cover half shells, and the like. The copolymers of this invention can be used in coatings.
25 Both interior and exterior surfaces of extrusion dies may be coated to, respectively, facilitate extrusion and alleviate die drip buildup.

Coated articles include gasoline engine carburetor parts; internal parts of internal combustion engines such as valves and piston skirts; razor blades; metal containers such as cans, pans, trays, vessels, and the like; metal sheets and foils;
30 continuous metal belts, metal rods, tubes, bars, profiles, and the like; bolts, nuts, screws, and other fasteners.

Coated articles include an article bearing a machine-readable marking on at least one surface, especially but not limited to a tag that can be attached to another object to provide information about inventory identification, contents, ownership,
35 hazards, operating conditions, or maintenance requirements, for example.

Coated articles include wire for electrical and mechanical service. In either case, the metal wire may be solid or stranded. Wires for mechanical service include catheter guide wire and the actuating wire of push-pull cable.

Coated articles include rubber o-rings, seals, beading, gasketing, fish hooks, and the like.

Coated articles include paper and textile materials, including woven fabric including glass fabric, non-woven fabric, felts, and the like, fibers including
5 filaments, yarns, e.g., staple and continuous filament, and strands.

Coated articles include foams, membranes, and the like.

Coated articles include optical fibers in which the substrate is a glass or plastic fiber.

Coated articles include semiconductors, semiconductor devices, magnetic
10 storage media including disks, photoconductors, electronic assemblies, and the like, wherein the coating thickness may be as little as 200 angstroms or even as little as 100 angstroms or even as little as 50 angstroms. Use of solutions containing low concentrations of the TFE/HFP copolymer of this invention, e.g., as low as 0.001 wt% copolymer can be especially advantageous to form these very
15 thin coatings.

One use for the TFE/HFP copolymers of this invention is as a processing aid in polyolefins. When the TFE/HFP copolymer of this invention is used as a processing aid in the polyolefin for film applications, the polyolefin generally will have a melt index (ASTM D-1238) of 5.0 or less at 190°C, preferably 2.0 or less.
20 For high-shear melt processing such as fiber extrusion or injection molding, even high-melt-index resins, for example, those having a melt index of 20 or more, may suffer processing difficulties. Such polyolefins may comprise any thermoplastic hydrocarbon polymer obtained by the homopolymerization or copolymerization of one or more monoolefins of the formula $\text{CH}_2=\text{CHR}'$ wherein R' is an alkyl radical,
25 usually of not more than eight carbon atoms. In particular, this invention is applicable to the following: polyethylene, both of the high-density type and the low-density type having densities within the range 0.89-0.97; polypropylene; polybutene-1; poly(3-methylbutene); poly(4-methylpentene); and linear low density copolymers of ethylene and an alpha-olefin, such as propylene, butene-1,
30 pentene-1, hexene-1, heptene-1, octene-1, decene-1, octadecene-1, or n-methylpentene-1.

Because of the different melt characteristics of the olefin polymers mentioned, the addition of the fluoropolymer process aids of this invention may be of greater value in some polyolefins than in others. Thus, polyolefins such as
35 polypropylene and branched polyethylene, that have low molecular weight or broad molecular weight distributions and, therefore, have good melt flow characteristics even at low temperature, may not require the use of the fluoropolymer additives or be noticeably improved by them, except under unusual, adverse extrusion conditions. However, for polymers such as high molecular weight, high density

polyethylene or linear low density ethylene copolymers, particularly those with narrow or very narrow molecular weight distributions, addition of the fluoropolymers is especially beneficial.

5 Such polyolefins are typically processed by extrusion techniques at melt processing temperatures T_p in the range of 175-275°C. The commercially important blown-film process is usually carried out at T_p in the range of 200-250°C, and commonly at 200-230°C.

10 The polyolefins and thus the polymer blend composition containing the fluoropolymer processing aid may contain assorted additives used in the art, such as but not limited to antioxidants, acid scavengers, light stabilizers, pigments, slip agents, and lubricants. In particular, finely divided solids such as silica or talc may be incorporated as antiblock agents.

15 The concentration of fluoropolymer processing aid in the host resin at fabrication into the final article should be high enough to achieve the desired effect in improving processibility, but not so high as to have adverse economic impact. The amount required can vary with the effect desired, the host resin, additives used in the host resin, and the processing conditions which may be different from the laboratory conditions reported in the following examples. Under certain conditions, concentrations of 100 ppm or less, as low as 50 ppm or even 25 ppm,
20 can be effective. Under other conditions, the effective amount may be 1000, 2000, or even 5000 ppm. For special purposes, concentrations of 10% or even 25% may be appropriate. Thus from about 25 ppm to about 25% by weight of the fluoropolymer may be present, with preferred ranges being from about 100 ppm to about 10% by weight, and even more preferable, about 100 ppm to about
25 2000 ppm by weight of the fluoropolymer. The fluoropolymer processing aid can be incorporated into the host resin at the desired final concentration, or can be incorporated into a masterbatch or concentrate that is added to the host resin in a ratio calculated to yield the desired final concentration.

30 A novel compound herein is $R^6R^7CFSO_2R^8$ wherein R^6 is perfluoroalkyl, perfluoroalkyl containing one or more ether oxygen atoms, perfluoroalkoxy or perfluoroalkoxy containing one or more ether oxygen atoms, R^7 is perfluoroalkyl or perfluoroalkyl containing one or more ether oxygen atoms, and R^8 is perfluoroalkyl. It is preferred that each of R^6 , R^7 and R^8 independently contain 1 to 30 carbon atoms. It is also preferred that R^8 is perfluoro-n-alkyl containing 1 to
35 20 carbon atoms. It is more preferred that R^6 is perfluoro-n-propoxy, R^7 is trifluoromethyl, and R^8 is perfluoro-n-octyl. This compound is useful as an initiator for the polymerizations described herein.

In the Examples, the ^{19}F NMR, which is used to determine the HFP distribution in the polymer, was measured on Bruker AC 250 NMR operating at

235 MHz. Polymer samples were loaded in 5 mm NMR tubes and heated to 250 to 360°C in a narrow bore probe. In the melt, the methine CF's of the HFP units appear at -183.5 ppm if present as isolated units, at -179.5 if present as head to tail diads, and at -177 ppm if present as head to tail triads. It is uncertain whether or not the integration for the HFP triads at -177 ppm also includes higher (than triads) oligomeric blocks. The amount of HFP triads was determined from the ratio of the areas of the ^{19}F NMR signal at -177 ppm to the total areas of the signals at -177, -179.5 and -183.5 ppm.

In the Examples, pressure change was used to calculate the weight of tetrafluoroethylene (TFE) added to the mixing reservoir (2). For the tetrafluoroethylene calculations in Examples 1-13, 50, 51 and 65, gauge pressure of TFE was incorrectly assumed to be absolute pressure. Based upon this incorrect assumption the quantity 160 g of TFE was shown for Examples 1-13, 50, 51 and 65. The actual TFE added in these Examples was about 217 g to 228 grams. The actual amounts of TFE that were added are shown and labeled as such in parenthesis in Examples 1 and 50, 51 and 65. The table on page 12 showing Examples 1-13 reflects the actual TFE measured.

In the Examples, the following abbreviations are used:

8CNVE - perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene)
20 Conv. - conversion
GPC - gel permeation chromatography
HFP - hexafluoropropylene
I.D. - inside diameter
IR - infrared (spectrum)
25 Mn - number average molecular weight
Mw - weight average molecular weight
Mv - viscosity average molecular weight
O.D. - outer diameter
PET - poly(ethylene terephthalate)
30 PMVE - perfluoro(methyl vinyl ether)
TFE - tetrafluoroethylene
TGA - thermogravimetric analysis
VF₂ or VF2 - vinylidene fluoride

In the Examples, the following materials are used:

35 "dimer" - a perfluorinated solvent which is defined in U.S. Patent 5,237,049
FC-40 - Fluorinert electronic liquid sold by 3M Industrial Chemicals
Division, thought to be substantially perfluoro(tributylamine).

FC®-75 - Fluorinert® Electronic Liquid, sold by 3M Industrial Chemicals Products Division, thought to be substantially perfluoro(2-butyl-tetrahydrofuran)

Kalrez® Perfluoroelastomer Parts - a tetrafluoroethylene/perfluoro(methyl vinyl ether) and curesite monomer copolymer part available from E. I. du Pont de Nemours and Company, Inc., Wilmington, DE, USA

Kapton® Polyimide Film - a polyimide film available from E. I. du Pont de Nemours and Company, Inc., Wilmington, DE, USA

Mylar® Polyester Film - a poly(ethylene terephthalate) film available from E. I. du Pont de Nemours and Company, Inc., Wilmington, DE, USA

Nordel® Hydrocarbon Rubber - an EPDM elastomer available from E. I. du Pont de Nemours and Company, Inc., Wilmington, DE, USA

PET - poly(ethylene terephthalate)

Viton® Fluoroelastomer - a copolymer of vinylidene fluoride and hexafluoropropylene available from E. I. du Pont de Nemours and Company, Inc., Wilmington, DE, USA

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic diagram of a High Pressure Continuous Unit which can be used for the continuous polymerization described herein. In Figure 1, within the barricade, NF_3 initiator is loaded into loop (1) and then blown to reservoir (2) using hexafluoropropylene (HFP). In (2) tetrafluoroethylene is added to the HFP/ NF_3 mixture, and the total mixture in (2) is then removed from the bottom of (2), boosted to a higher pressure and recirculated through the Monomer Recycle Loop, and then part of it is sent to the heated (polymerization) reactor (5) and part of it is recycled through valve (4) back to (2) after the pressure is lowered at pressure regulator (3) to the pressure of the contents of (2). After exiting reactor (5), the pressure of the mixture is reduced (often to atmospheric pressure) at back pressure regulator (6) and the copolymer product is isolated in glass collection bottle (7). Gaseous matter leaving the collection bottle is passed through meter (8) which is used to measure the amount of unreacted gaseous monomers. A more detailed description of the use of the apparatus of Figure 1 appears below.

EXAMPLE 1

Continuous Polymerization in 10 ml Autoclave with Agitation

All the reactants needed for a single run were premixed in a reservoir, pressured to 103 MPa, bled off through a heated pressure vessel at slightly lower pressure, and finally vented to atmospheric pressure in the form of solid polymer foamed with unreacted monomer. The detailed procedure given below for Example 1 is in reference to the reactor schematic, Figure 1.

Preparation of Homogeneous Monomer/Initiator Mix

A 25 ml loop (1) off the feed line to a 3.8 L reservoir (2) was pressured to 710 kPa with nitrogen trifluoride at ambient temperature (~0.6 g of NF_3). The 3.8 L reservoir was then loaded with 160 g of TFE (actual TFE loaded was 222 g) and 4000 g of HFP, a portion of the HFP being used to blow the NF_3 into the reservoir (2). Liquid monomer phase was pulled off the bottom of the reservoir, pressured to 103 MPa, and then recirculated back to the reservoir via back pressure regulator (3). The run was not started until the contents of theclave had been mixed by 10 minutes of such recirculation. Recirculation through the reservoir was maintained for the duration of the run. No effort was made to control the temperature of the reservoir which varied in the case of this run from 23°C at the start to 33°C at the finish.

Monomer Feed to Reactor

Flow was maintained through the system by letting monomer pressure down in stages, from 103 MPa in the recirculation loop to 96.5 MPa in the reactor and finally to atmospheric pressure in the product collector. The rate of flow was controlled by a micrometering valve (4) in the stainless steel line that connected the reservoir recirculation loop at 103 MPa with the reactor at 96.5 MPa. Reactor pressure was maintained at 96.5 MPa by back pressure regulator (6) placed after reactor (5). Micrometering valve (4) was opened until monomer flowed through the reactor at 10 to 12 g per minute, the measurement of flow rates being discussed later. In order to maintain steady flow throughout the run, periodic adjustments were made to micrometering valve (4).

Reactor

As already mentioned, a flexible stainless steel tube, 0.40 cm O.D. by 0.16 cm I.D., was run from micrometering valve (4) to the front end of reactor (5). In an effort to bring the monomers up to reactor temperature rapidly, the last ~61 cm of tubing before the reactor was wrapped with electrical tape and preheated to ~200°C. Considering that the internal volume of this preheated segment is small relative to the reactor proper (~1 ml in the preheated line vs.

10 ml in the reactor) and that reaction rates are slower at 200°C than at 275°C, polymer formation in the preheated line was ignored for the purposes of productivity calculations. Reactor (5), in this Example a 10 cc stainless steel autoclave (10.2 cm long X 1.1 cm I.D. and containing two loose 0.63 cm stainless steel balls), was rocked vigorously with a paint shaker while heating to 275°C.

Product Isolation

A piece of flexible stainless steel tubing was run from reactor (5) to back pressure regulator (6) at which point pressure was dropped from 96.5 MPa to atmospheric. In spite of the fact that no effort was made to warm either the line or the valve, no plugging was observed in this and the majority of runs. When plugging did occur, it was most often at the low pressure side of the regulator (6) where foamed polymer was left when the monomer flashed off. To minimize plugging, the low pressure side of the let down valve was drilled out to provide as large an orifice as possible and then connected directly to a several liter glass collection bottle (7). Gaseous monomer exiting the glass collection bottle was passed through wet test meter (8), the liters of monomer per minute being converted to monomer flow in grams per minute. An average flow rate of 10.9 g/min was thus observed over the 247 minute duration of this run. Given that the density of HFP at 275°C/96.5 MPa is ~1.29 g/ml, the average residence time for the monomers in reactor (5) was ~1.2 minutes. Polymer was recovered from the glass collection bottle (7) as large chunks of foamed white solid weighing 170.2 g. Pulling residual monomer off with a vacuum pump reduced the weight of polymer to 159 g for a productivity of 3.8 kg/L/hr. Fluorine NMR of the polymer melt at 330°C found 43 mole % (53 wt %) HFP copolymerized with 57 mole % (47 wt %) TFE, allowing the calculation of 54% TFE conversion per pass and 3.2% HFP conversion per pass. Rolling 1.5 g of this polymer with 5 ml of FC-75 at room temperature gave a viscous solution. Transparent films were pressed at 160°C by applying 3600 kg of pressure for 1 minute to 1 g samples held between Kapton® polyimide film cover sheets. Under an applied weight of 15 kg, a 2 g sample extruded through a melt indexer at 0.63 g/minute at 200°C. GPC in FC-75 solvent showed $M_w=235,000$ and $M_n=94,700$ for a $M_w/M_n=2.87$.

Characterization Summary

The results of Example 1 as well as of Examples 2 to 13 made under the same conditions are tabulated below. Reproducibility was excellent considering that the process has yet to be automated.

Ex.	Residence Time	Polymer		Conv. Per Pass		kg/L/hr	Mw/Mn ³	η_{inh} ⁴
		Wt % HFP ¹	Melt Index ²	HFP	TFE			
1	1.2 min	53%	0.6 g/min	3.2%	54%	3.8	2.87	0.39
2	0.9 min	45%	0.4 g/min	2.4%	54%	4.2	3.65	0.45
3	1.0 min	50%	0.3 g/min	2.6%	50%	3.9	3.53	0.54
4	0.9 min	49%	0.5 g/min	2.2%	45%	3.7	3.63	0.49
5	1.0 min	51%	0.4 g/min	2.5%	46%	3.8	3.23	0.49
6	1.0 min	51%	0.6 g/min	2.7%	50%	3.9	3.34	0.51
7	1.0 min	51%	1.3 g/min	2.6%	47%	3.8	3.12	0.41
8	1.0 min	50%	0.7 g/min	2.5%	48%	3.6	2.99	0.44
9	1.0 min	54%	1.0 g/min	2.7%	44%	3.6	3.83	0.29
10	1.1 min	53%	0.7 g/min	3.1%	52%	3.8	2.85	0.41
11	1.2 min	50%	0.8 g/min	3.1%	55%	3.7	2.62	0.39
12	1.1 min	53%	0.7 g/min	2.8%	47%	3.5	2.45	0.48
13	1.2 min	53%	1.0 g/min	3.1%	53%	3.6	2.57	0.41

¹Composition determined by fluorine NMR in the melt at 300-340°C

²Melt index determined at 200°C with a 15 kg weight

³Mw and Mn determined by GPC using FC-75 solutions, versus linear poly(hexafluoropropylene oxide) standards, one with Mn ~20,000, the other with Mn ~70,000

⁴Inherent viscosity in FC-75

COMPARATIVE EXAMPLE 1

An 85 ml autoclave was loaded with 60 ml of perfluorodimethylcyclobutane and 0.25 g of cobalt trifluoride. The autoclave was sealed, chilled, and evacuated. Hexafluoropropylene was used to sweep in 4.25 g of TFE.

- 5 Enough HFP was added to bring the pressure of the autoclave to 930 MPa at 23°C (~30 g of HFP). The autoclave was heated to 199°C and 296 MPa, an additional 6.9 MPa of HFP being added to match Eleuterio's condition of 303 MPa. The autoclave was held at ~200°C for four hours and then cooled and vented. The resulting polymer solution was filtered to get rid of pink residues (presumably
- 10 containing insoluble cobalt compounds), stripped to heavy oil on a rotary evaporator and then blown down to 0.94 g of solid using a stream of nitrogen. This solid has an inherent viscosity of 0.207 in FC-75 closely matching Eleuterio's Example II. Mw/Mn was 6.39, a very broad molecular weight distribution compared to polymers made by our process. In a TGA analysis, this polymer had
- 15 lost 20% of its weight by 340°C.

Ex.	Residence Time	Polymer	Melt Index	Conv. Per Pass		kg/L/hr	Mw/Mn
		Wt % HFP		HFP	TFE		
Com. 1	240 min	57%	--	--	--	0.02	6.39

EXAMPLES 14 TO 19**Continuous Polymerization in 10 mL Autoclave.****With and Without Agitation**

5 The same set up was used as in Examples 1 to 13. About 80 to 90 grams
TFE, 200 g HFP and 0.6 g NF₃ were loaded to the mixingclave, making the ratio
of initiator relative to monomer about twice as great as in Examples 1 to 13, and
reactor temperature was 300 to 325°C instead of 275°C. In all Examples but 14
10 the reactor was agitated by vigorous rocking. Product characterizations are shown
below.

Ex.	Residence Time	Polymer	Melt Index ²	Conv. Per Pass		kg/L/hr	Mw/Mn ³
		Wt % HFP ¹		HFP	TFE		
NO SHAKING, 300°C							
14	0.9 min.	51%	2 g/min	2.7%	64%	3.9	3.57
SHAKING, 300°C							
15	0.5 min.	46%	20 g/min	1.2%	36%	4.0	2.79
16	0.7 min.	56%	2 g/min	2.7%	52%	4.4	2.12
17	0.9 min.	55%	20 g/min	4.1%	84%	5.5	3.60
18	1.9 min.	60%	20 g/min	5.4%	91%	3.2	2.41
SHAKING, 325°C							
19	0.9 min.	60%	4 g/min	5.3%	86%	6.4	2.38

¹Composition determined by fluorine NMR in the melt at 300-340°C

²Ex. #14 melt index at 200°C with 15 kg weight

Ex. #15 melt index at 200°C with 15 kg weight

Ex. #16 melt index at 200°C with 15 kg weight

Ex. #17 melt index at 200°C with 15 kg weight

Ex. #18 melt index at 200°C with 15 kg weight

Ex. #19 melt index at 200°C with 5 kg weight

³Mw and Mn determined by GPC using FC-75 solutions, versus linear poly(hexafluoro-propylene oxide) standards, one with Mn=20,000, the other with Mn=70,000

EXAMPLES 20 TO 44**Continuous Polymerization in Tube, No Agitation**

15 The same set up was used as for Examples 1 to 13, except that in these
Examples reactor (5) was a 0.95 cm OD x 0.52 cm ID x 5.3 m long coil of
stainless steel tubing with an internal volume of ~110 ml. The reactor coil was

heated using a sand bath. In view of the 5.3 m length of the tube no preheater was needed. Results for Examples 20 to 44 are shown in the table below. Example 43 was unique in that 435 ml of liquid FC-75 was added along with the initial monomer charge. The result of doing this is that the product was obtained as

5 ~400 ml of solution containing 0.16 g of dissolved polymer/ml.

Ex.	°C	MPa	Res. Time	Weight % HFP		% Conversion		kg/L/hr
				Feed	Polymer ¹	HFP	TFE	
~CONSTANT T, P, AND FEED								
20	250°C	75.8	21 min.	98%	64%	2.9	81	0.2
21	250°C	75.8	9 min.	98%	61%	2.2	72	0.3
22	250°C	75.8	5 min.	98%	59%	2.2	76	0.5
23	250°C	75.8	4 min.	98%	58%	1.5	55	0.7
24	250°C	75.8	3 min.	98%	58%	1.3	37	0.6
CONSTANT T, P, AND ~TIME								
25	250°C	96.5	6 min.	98%	58%	2.3	84	0.6
26	250°C	96.5	6 min.	96%	53%	3.8	84	0.9
27	250°C	96.5	6 min.	96%	54%	3.4	72	0.9
28	250°C	96.5	6 min.	96%	52%	3.2	74	0.9
29	250°C	96.5	6 min.	96%	53%	3.8	86	1.0
30	250°C	96.5	6 min.	95%	50%	4.3	80	1.1
31	250°C	96.5	6 min.	94%	44%	2.9	56	0.8 ²
32	250°C	96.5	8 min.	92%	47%	4.6	63	0.9 ²
CONSTANT P, FEED, AND ~TIME								
33	275°C	75.8	18 min.	98%	67%	3.3	85	0.2
34	250°C	75.8	21 min.	98%	64%	2.9	81	0.2
35	225°C	75.8	21 min.	98%	57%	1.7	65	0.1
36	325°C	96.5	6 min.	96%	59%	5.1	89	1.1
37	300°C	96.5	5 min.	96%	56%	5.4	~100	1.4
38	275°C	96.5	7 min.	96%	59%	5.2	90	1.0
39	250°C	96.5	6 min.	96%	53%	3.8	84	0.9
CONSTANT T, FEED, AND ~TIME								
40	250°C	62.0	5 min.	98%	59%	1.9	65	0.5
41	250°C	75.8	5 min.	98%	59%	2.2	76	0.5
42	250°C	96.5	6 min.	98%	60%	2.3	75	0.6
IN THE PRESENCE OF FC-75 SOLVENT AND THIRD MONOMER, 8CNVE								
43	250°C	96.5	~6 min.	90+ ³	64% ³	2.3	31	0.4

IN THE PRESENCE OF THIRD MONOMER. PMVE

44	250°C	96.5	~6 min.	94% ⁴	47% ⁴	3.1	~100	0.9
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¹Composition determined by fluorine NMR in the melt at 300-340°C²Incomplete removal of polymer from reactor, kg/L/hr probably larger than reported³Several percent 8CNVE, $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ in feed. Polymer composition by fluorine NMR: 63.8 wt % HFP, 34.1 wt % TFE, 2.1 wt % 8CNVE⁴Starting mix: 94.3% wt % HFP, 3.8 wt % TFE, 1.9 wt % PMVE
Polymer: 37.2 mole % HFP, 60.7 mole % TFE, 2.1 mole % PMVE

Molecular weight distributions were measured for only a few of the samples made in the tubular reactor. Distributions appear to be a bit broader and less uniform than experienced in the shaken autoclave (Examples 1-13 and 15-19) or the well-stirred reactor (Example 85).

Example	Mw/Mn
38	4.96
27	3.20 avg. of 2
28	3.93 avg. of 2
29	3.48 avg. of 2

EXAMPLES 45 TO 49Continuous Polymerization in Tube. No AgitationEffect of Decreasing Initiator

The same tubular reactor as described in Examples 20 to 44 was run at 250°C/96.5 MPa with a residence time of 5.6 to 6.0 minutes and 2500 g HFP + 50 g TFE + a variable amount of NF_3 added to the 3.8 L mixing reservoir. The effects of varying the amount of NF_3 in the starting monomer mix is shown below.

Ex.	Estimated Grams NF_3 in Feed ¹	Wt % HFP		% Conversion		Kg/L/hr
		Feed	Polymer	HFP	TFE	
45	0.7 g	98%	58%	2.3	84	0.6
46	0.4 g	98%	58%	1.6	56	0.4
47	0.2 g	98%	60%	1.8	62	0.4
48	0.1 g	98%	58%	1.5	54	0.3
49	None	98%	57%	0.7	28	0.2

¹The grams of NF_3 added to the monomer mixing reservoir were estimated from $PV = nRT$. The amount of NF_3 delivered to the reactor for polymerization, however, may be quite a bit less if the highly volatile NF_3 concentrates in the vapor phase rather than in the liquid monomer phase that is pumped to the reactor.

Initiation in the absence of NF_3 is probably the result of adventitious oxygen. Shown immediately below are the results of ^{19}F NMR analyses giving the

percentages of HFP repeat units which are isolated, in diads and in triads for certain Examples.

Example #	Wt. % HFP	% of Total CF's Found in Polymer by ¹⁹ F NMR		
		Triads	Diads	Isolated
34	67%	12.40	41.47	46.13
35	64%	15.86	39.42	44.72
23	59%	9.06	36.72	54.22
36	57%	9.92	35.59	54.49
33	47%	5.56	25.53	68.91
Comparative Example #1	57%	26.63	27.26	46.4

5

EXAMPLE 50

The agitated reactor was set up as in Example 1. Instead, however, of using NF₃ as the initiator, a solution of 0.8 ml of perfluorodibutylamine [(C₄F₉)₂NF] dissolved in 5 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced directly in the 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 160 g of TFE (actual TFE loaded was 223 g) and 4000 g of HFP was run through the 10 ml agitated reactor at ~12 g/min at 275°C (estimated residence time 1 minute) and 96.5 MPa for 315 minutes. This gave 146 g of poly(HFP/TFE), for a productivity of 2.8 kg/L/hr. The polymer was soluble in FC-75 and found to have Mw=603,000, Mn=226,000, and Mv=546,000. Fluorine NMR in the melt at 340°C found 49 wt % HFP, 51 wt % TFE, and 74% of the methine FC's as triads. Conversion per pass was 38% for TFE and 1.9% for HFP.

EXAMPLES 51-55

The agitated reactor was set up as in Example 1. Instead, however, of using NF₃ as the initiator, a solution of 1.5 g of perfluorodibutylamine [(C₄F₉)₂NF] dissolved in 5 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced directly in the 96.5 MPa reservoir 2 prior to the start of the run. A mix of the initiator with 160 g of TFE (actual TFE loaded was 222 g) and 4000 g of HFP was run through the 10 ml agitated reactor at 9.5 g/min at 325°C (estimated residence time 1.2 min) and 96.5 MPa for 365 minutes. This gave 239 g of poly(HFP/TFE), for a productivity of 4.0 kg/L/hr. The polymer was soluble in FC-75. Fluorine NMR in the melt at 320°C found 54 wt % HFP/46 wt % TFE with 6.1% of the HFP methines as triads. GPC in FC-75 found Mw=348,000, Mn=130,000, Mv=304,000. Inherent viscosity in FC-75 was 0.413. Per pass conversions were 63% for TFE and 3.8% for HFP.

- A major difference between NF_3 and $(\text{C}_4\text{F}_9)_2\text{NF}$ is that $(\text{C}_4\text{F}_9)_2\text{NF}$ is a relatively nonvolatile liquid. This means that when a mix of HFP, TFE, and $(\text{C}_4\text{F}_9)_2\text{NF}$ is made in mixing reservoir 2, almost all of the $(\text{C}_4\text{F}_9)_2\text{NF}$ will reside in the liquid monomer phase. This in turn allows us to estimate with moderate accuracy how much $(\text{C}_4\text{F}_9)_2\text{NF}$ was actually used as an initiator in this run: when 3472 g out of 4223 g (82%) of starting monomer mix was pumped through reactor 5, a like fraction of the $(\text{C}_4\text{F}_9)_2\text{NF}$, 82% or about 1.23 g, was probably used to initiate polymerization. Knowing that 1.23 g of $(\text{C}_4\text{F}_9)_2\text{NF}$ initiated 239 g of polymer with $M_n=130,000$ and assuming that there are two $(\text{C}_4\text{F}_9)_2\text{NF}$ derived end groups per chain allows one to calculate that each $(\text{C}_4\text{F}_9)_2\text{NF}$ generated in fact 1.4 radicals. Generating 1.4 radicals out of a potential maximum of 2 [$\text{F}\cdot$ and $(\text{C}_4\text{F}_9)_2\text{N}\cdot$] represents an initiator efficiency of 70% for $(\text{C}_4\text{F}_9)_2\text{NF}$ at 325°C . A similar calculation for Example 50 above shows that the efficiency of $(\text{C}_4\text{F}_9)_2\text{NF}$ drops to about 24% at 275°C .
- Properties of the $(\text{C}_4\text{F}_9)_2\text{NF}$ initiated polymer made here in Example 51 are compared to those of closely bracketing NF_3 initiated runs (Examples 52 to 55) made in the same equipment:

Ex. #	Gel Permeation Chromatography Data				IV	^{19}F NMR DATA	
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$M_v \times 10^{-3}$		Wt% HFP	Triads
52	334	129	2.59	292	0.411	53% HFP	6.5%
51	348	130	2.67	304	0.413	54% HFP	6.1%
53	371	142	2.99	326	0.443	50% HFP	5.3%
54	423	137	3.08	367	0.492	51% HFP	5.0%
55	451	156	2.90	397	0.517	48% HFP	3.2%

20

EXAMPLE 56

- The agitated reactor was set up as in Example 1. Instead, however, of using NF_3 as the initiator, 76 kPa (gauge) of CF_3OOCF_3 (about 0.3 g) was introduced into a 25 ml initiator loop 1. A mix of this initiator with 160 g of TFE (actual TFE loaded was 221 g) and 4000 g of HFP was run through the 10 ml agitated reactor at about 10.6 g/min at 275°C and 96.5 MPa for 340 minutes. This gave 53 g of poly(HFP/TFE), for a productivity of 1.0 kg/L/hr. The polymer was soluble in FC-75 and found to have $M_w=852,000$ and $M_n=235,000$.

EXAMPLE 57

- A 50 wt % HFP copolymer of HFP and TFE, which had a melt viscosity at 100 sec^{-1} of 854 Pa-s was dissolved in a variety of solvents to test solubility. To an Erlenmeyer flask fitted with a reflux condenser and magnetic stirrer were added 95 g various solvents and 5 g polymer. The mixtures were heated on a hot plate

with stirring until reflux occurred. The solvents tested were "dimer", FC-75, FC-40 and hexafluorobenzene.

The polymer dissolved in all solvents tested to form clear, low viscosity solutions. When cooled to room temperature, all samples remained as clear, low viscosity fluids.

EXAMPLE 58

The FC-75 solution of Example 57 was used to prepare dipped coatings on various metals. Metal coupons of size 2.5 cm x 7.6 cm x 0.64 mm were cleaned in an ultrasonic bath with acetone, dried at 150°C for 4 hours, cooled to room temperature and dipped into the 5% solution. Excess solution was drained off. The coupons were dried overnight at 150°C. Metals tested were copper, brass, aluminum, stainless steel, galvanized steel and chrome plated steel. All coatings were smooth and clear. The copper coupon had some discoloration.

Contact angle measurements of a droplet of water on each coating were made. Contact angles were 115° +/- 2° advancing and 94° +/- 2° receding, showing that the coatings were uniform and were hydrophobic.

Film thickness was measured for each coupon using a Tencor Stylus Profilometer. Film thickness was 1.7 µm +/- 0.5 µm.

Film adhesion was tested using ASTM D3359. Each coated film was scratched in a cross hatch pattern of 10 lines per 2.5 cm using a razor knife edge. Adhesive tape was pressed against the cross hatch scored film. The tape was removed and the film examined. No removal of polymer film from the metal coupon occurred. The cross hatched scored coated films were placed in boiling water for 1 hour. The coupons were removed from the water, dried at 150°C for 1 hour and were cooled to room temperature. An adhesive tape was again pressed against the cross hatch scored film and then removed. No removal of polymer film from the metal coupon occurred. This shows that the coated films are strongly adhered to the metal coupons and can resist the action of boiling water.

EXAMPLE 59

The FC-75 solution of Example 57 was used to prepare dipped coatings on various polymers. Polymer strips of size 2.5 cm x 7.6 cm x 1.9 mm were prepared from nylon 6,6, Nordel® hydrocarbon rubber vulcanizate, neoprene vulcanizate, Viton® fluorocarbon rubber vulcanizate, Kalrez® perfluorocarbon rubber vulcanizate, and strips of size 2.5 cm. x 7.6 cm x 0.25 mm were cut from films of Mylar® PET and Kapton® polyimide (all of these products are available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A.). All samples were cleaned in an ultrasonic bath with acetone, dried at 150°C for 4 hours, cooled to room temperature and dipped into the 5% solution. Excess solution was

drained off. The coated samples were dried overnight at 150°C. All coatings were smooth and clear.

Contact angle measurements of a droplet of water on each coating were made. Contact angles were 115° +/- 4° advancing and 94° +/- 4° receding, showing that the coatings were uniform and were hydrophobic.

Film thickness was measured for coatings on nylon, Mylar® and Kapton® using a Tencor Stylus Profilometer. Film thickness was 1.7 µm +/- 0.5 µm.

Film adhesion was tested using ASTM D3359. Each coated film was scratched in a cross hatch pattern of 10 lines per 2.5 cm using a razor knife edge. Adhesive tape was pressed against the cross hatch scored film. The tape was removed and the film examined. No removal of the coated film from the polymer surface occurred. The cross hatch scored coated strips were placed in boiling water for 1 hour. The strips were removed from the water, dried at 150°C for 1 hour and were cooled to room temperature. An adhesive tape was again pressed against the cross hatch coating and then removed. No removal of coating film from the polymer strips occurred. This shows that the coated films are strongly adhered to the polymer strips and can resist the action of boiling water.

EXAMPLE 60

The solution of Example 57 in FC-75 was used to prepare dipped coatings on various fabrics. Pieces of fabric were cut to size 15.2 cm square. The fabrics were a loose woven nylon, a loose woven PET polyester, a loose woven cotton and a Nomex® felt. The fabrics were dipped into the 5% solution and were squeezed by hand to remove excess solution. The fabrics were dried for 1 hour at 150°C. After drying, all fabrics remained soft and flexible and were porous.

A drop of distilled water was placed on each fabric and on a portion of the same fabric that had not been treated. In each case, the water wet and penetrated the untreated fabric, but formed a spherical drop on the treated fabric and did not penetrate. Thus, the treated fabrics were hydrophobic.

EXAMPLE 61

The solution of Example 57 in FC-75 was treated as a mold release agent. A size 214 O-ring mold was cleaned with Easy Off® commercial oven cleaning agent. The mold was washed with water and dried by heating in a press at 177°C for 15 min. The mold had 30 sites for molding O-rings. Fifteen sites were spray coated with solution. The remaining sites were coated with commercial mold release, McLube® No. 1725. The coatings were dried by placing the mold in a press at 177°C for 15 min. Kalrez® O-ring preforms were placed in the proper sites and the mold was placed in a press at 177°C for 15 min to mold the O-rings.

After the first molding cycle there was some sticking to the McLube coated sites. The solution coated sites had no sticking. The mold cycle was repeated for three additional cycles with no additional mold release coating applied to any of the sites. After the final molding cycle, about 30% of the O-rings removed from the sites lubricated with McLube® were torn during removal from the mold due to sticking. None of the O-rings removed from sites coated with solution were torn. There was no sticking of O-rings at the solution coated sites.

EXAMPLE 62

The solution of Example 57 in FC-75 was tested as a mold release agent. A conventional golf ball compression mold was cleaned with "Easy Off" commercial oven cleaning agent. The mold was washed with water and dried by heating in a press at 204°C for 15 min. The mold was spray coated with solution and was dried by placing the mold in a press at 204°C for 4 hours. The mold cavity was filled with a Surlyn® ionomer golf ball cover and a spiral wound rubber core. The golf ball was compression molded for 15 min at 204°C.

When the mold was used without solution coating, the golf ball cover adhered to the metal mold and pulled away from the core when the ball was removed from the mold. When the mold was coated with the solution there was no sticking and the molded golf ball was easily removed.

EXAMPLE 63

A linear low density polyethylene with melt index 1 g/10 min was extruded through a capillary die of size 0.76 mm x 2.5 cm x 90° using an Instron® capillary rheometer. The shear stress required to extrude the polyethylene at 220°C at a shear rate of 347 sec⁻¹ was 4.0 x 10⁵ Pa. The surface of the extrudate was rough and distorted.

To the polyethylene was added TFE/HFP copolymer at a level of 0.1%. The extrusion through the capillary die was repeated. When the polyethylene containing the TFE/HFP copolymer was extruded at 220° at a shear rate of 347 sec⁻¹ the shear stress required was reduced to 2.0 x 10⁵ Pa, and the extrudate was smooth and was not distorted. Thus, the presence of the copolymer reduced the shear stress required to extrude the polyethylene from 4.0 x 10⁵ Pa to 2.0 x 10⁵ Pa and the surface of the extrudate became smooth and undistorted. The TFE/HFP copolymer acted as a processing aid for the polyethylene.

EXAMPLE 64

An 0.38 mm x 9.5 mm x 90° tungsten carbide capillary was coated with a 1% solution of TFE/HFP copolymer dissolved in FC-75. The coating was dried at 250°C for 2 hours. A linear low density polyethylene, GRSN 7047 from Union Carbide Corp., melt index 1 g/10 min, containing 2.5% colloidal silica (to act as an

abrasive material) was extruded through the capillary die using an Instron capillary rheometer at a temperature of 220°C and at a shear rate of 833 sec⁻¹.

When the polyethylene was extruded through the capillary die with no solution coating on the capillary, at a temperature of 220°C and at a shear rate of 833 sec⁻¹ the shear stress required was 4.5×10^5 Pa. The surface of the extrudate was rough and distorted. When the polyethylene was extruded through the coated capillary under the same conditions, the shear stress required dropped to 2.5×10^5 Pa shortly after start up and the surface of the extrudate was smooth and undistorted. The shear stress slowly rose, over a period of about 2 hours to 4.5×10^5 Pa, as the solution coating was slowly worn away by the abrasive polyethylene. When the shear stress reached a level greater than 3.0×10^5 Pa the surface of the extrudate again became rough. This example shows that the solution coating on the capillary acted as an extrusion aid that significantly reduced shear stress and eliminated surface roughness. When the coating was completely worn away, after two hours, the shear stress returned to the uncoated value and surface roughness reappeared.

EXAMPLE 65

Polymerization in Presence of CO₂

The agitated reactor was set up as in Example 1, loading a mixture of 3000 g of HFP, 160 g of TFE (actual: 226), 157 g of CO₂ diluent, and 1.5 g of NF₃. This mixture was run through the 10 cc agitated reactor at about 10 to 11 g/min at 300°C and 96.5 MPa for 278 minutes. This gave 254 g of polymer for a productivity of 5.5 kg/L/hr. The polymer had an inherent viscosity of 0.254 and a melt flow of 4 g/min at 200°C under a load of 5 kg in a melt indexer.

EXAMPLES 66-84

Polymerizations in Examples 66 to 84 here were run in a semicontinuous fashion using the equipment and general methods described in Example 1. Initiator performance is compared in terms of grams of polymer made per gram of initiator. For this is used the formula: (grams of polymer) ÷ [(grams of initiator added to the mixingclave) X (fraction of reaction mixture run through the polymerizer)]. Polymerization temperatures were measured using a thermocouple placed between the wall of the reactor and its heating jacket except in Example 85 in which case reactor temperature was measured internally. Example 85 also changes the reactor from a shaken tube to a larger, mechanically well-stirred vessel with separately metered flows for the HFP, the TFE, and a HFP/NF₃ mixture. The larger scale and the use of calibrated flow meters in Example 85, should make monomer feed ratios more accurate.

EXAMPLE 66**CF₃CF₂CF₂C(CF₃)₂NF₂ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml CF₃CF₂CF₂C(CF₃)₂NF₂ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 114 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 275°C (estimated residence time 1.2 min) and 96.5 MPa for 154 minutes. After vacuum pump drying at room temperature, this gave 51.1 g of poly (HFP/TFE) for a productivity of 2.0 kg/L/hr. One gram of polymer was soluble in 5 ml of room temperature FC-75 with a trace of insoluble haze. Fluorine NMR in the melt at 320°C found 44 wt % HFP/56 wt % TFE with 1.3% of the HFP methines as triads. GPC in FC-75 at 80°C found Mw = 629,000, Mn = 251,000, Mv = 566,000. Inherent viscosity in FC-75 at 25°C was 0.365. Roughly 69 g of polymer were made/g of CF₃CF₂CF₂C(CF₃)₂NF₂ initiator.

EXAMPLE 67**(CF₃)₂CFN=NCF(CF₃)₂ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.3 ml (CF₃)₂CFN=NCF(CF₃)₂ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 115 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 145 minutes. After vacuum pump drying at room temperature, this gave 77.6 g of poly (HFP/TFE) for a productivity of 3.2 kg/L/hr. One gram of polymer gave a hazy, quite viscous solution in 5 ml FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 53 wt % HFP/47 wt % TFE with 8.3% of the HFP methines as triads. GPC in FC-75 at 80°C found Mw = 599,000, Mn = 229,000, Mv = 541,000. Inherent viscosity in FC-75 at 25°C was 0.540. Roughly 195 g of polymer were made per gram of (CF₃)₂CFN=NCF(CF₃)₂ initiator.

EXAMPLE 68**(CF₃)₂CFN=NCF(CF₃)₂ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.6 g (CF₃)₂CFN=NCF(CF₃)₂ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 114 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 12 g/min at 275°C (estimated residence time 1.1 min) and 96.5 MPa for 160 minutes. After

- vacuum pump drying at room temperature, this gave 59.7 g of poly (HFP/TFE) for a productivity of 2.2 kg/L/hr. The polymer was soluble in FC-75. Fluorine NMR in the melt at 275°C found 46 wt % HFP/54 wt % TFE with 2.1% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 477,000$, $M_n = 124,000$, $M_v = 413,000$. Inherent viscosity in FC-75 at 25°C was 0.614. Roughly 110 g of polymer were made per gram of $(CF_3)_2CFN=NCF(CF_3)_2$ initiator.

EXAMPLE 69 **$(CF_3)_2CFN=NCF(CF_3)_2$ Initiation**

- The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.5 ml $(CF_3)_2CFN=NCF(CF_3)_2$ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 116 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 275°C (estimated residence time 1.2 min) and 96.5 MPa for 110 minutes. After vacuum pump drying at room temperature, this gave 50.5 g of poly (HFP/TFE) for a productivity of 2.7 kg/L/hr. One gram of polymer in 5 ml of room temperature FC-75 gave a highly viscous, hazy solution in FC-75 with perhaps significant amounts of polymer still present as swollen gel. Fluorine NMR in the melt at 340°C found 48 wt % HFP/52 wt % TFE with 5.0% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 569,000$, $M_n = 185,000$, $M_v = 508,000$. Inherent viscosity in FC-75 at 25°C was 0.557. Roughly 95 g of polymer were made per gram of $(CF_3)_2CFN=NCF(CF_3)_2$ initiator.

EXAMPLE 70**N-Fluoroperfluoropiperidine Initiation**

- The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.3 ml N-fluoroperfluoropiperidine dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 115 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 14 g/min at 350°C (estimated residence time 0.8 min) and 96.5 MPa for 110 minutes. After vacuum pump drying at room temperature, this gave 100.2 g of poly (HFP/TFE) for a productivity of 5.4 kg/L/hr. The polymer was soluble in FC-75. Fluorine NMR in the melt at 340°C found 50 wt % HFP/50 wt % TFE with 2.6% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 445,000$, $M_n = 181,000$, $M_v = 398,000$. Inherent viscosity in FC-75 at 25°C was 0.461. Roughly 230 g of polymer were made per gram of N-fluoroperfluoropiperidine initiator.

EXAMPLE 71**CF₃C(C₂F₅)₂CF(CF₃)₂ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 1.0 ml CF₃C(C₂F₅)₂CF(CF₃)₂ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 113 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 10 g/min at 350°C (estimated residence time 1.1 min) and 96.5 MPa for 106 minutes. After vacuum pump drying at room temperature, this gave 105.6 g of poly (HFP/TFE) for a productivity of 6.0 kg/L/hr. One gram of polymer gave a clear, attractive solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 58 wt % HFP/42 wt % TFE with ~7% of the HFP methines as triads. GPC in FC-75 at 80°C found Mw = 199,000, Mn = 93,000, Mv = 179,000. Inherent viscosity in FC-75 at 25°C was 0.247. Approximately 100 g of polymer were made per gram of CF₃C(C₂F₅)₂CF(CF₃)₂ initiator.

Running an identical polymerization but at 275°C gave 73.4 g of polymer after 145 minutes with an average monomer flow rate of 11 g/min. This polymer analyzed for 50 wt % HFP/50 wt % TFE and 5.5% triads by fluorine NMR at 320°C; Mw = 239,000, Mn = 82,900, and Mv = 206,000 by GPC; inherent viscosity = 0.391 at 25°C; and a productivity of 3.0 kg/L/hr. Roughly 51 g of polymer were made per gram of initiator.

*CF₃C(C₂F₅)₂CF(CF₃)₂: 88% CF₃C(C₂F₅)₂CF(CF₃)₂ and 12% [(CF₃)₂CF]₂CFCF₂CF₃ which is assumed to be an inactive component

EXAMPLE 72**[(CF₃)₂CF]₂C=CFCF₃ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 2.0 ml [(CF₃)₂CF]₂C=CFCF₃*, dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane), was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 116 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 10 g/min at 350°C (estimated residence time 1.2 min) and 96.5 MPa for 112 minutes. After vacuum pump drying at room temperature, this gave 34.4 g of poly (HFP/TFE) for a productivity of 1.8 kg/L/hr. The polymer gave a highly viscous, hazy solution in FC-75. Fluorine NMR in the melt at 225°C found 52 wt % HFP/48 wt % TFE with 2.5% of the HFP methines as triads. Inherent viscosity in FC-75 at 25°C was 0.806. Roughly 16 g of polymer were made per gram of initiator.

*[(CF₃)₂CF]₂C=CFCF₃: 25% [(CF₃)₂CF]₂C=CFCF₃, 72.5% [(CF₃)₂CF](C₂F₅)C=C(CF₃)₂, 1.5% [(CF₃)₂CF]CF=C(CF₃)(CF₂CF₂CF₃)

EXAMPLE 73**C₂F₅SO₂C₂F₅ Initiation**

A. Initiation at 275°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml C₂F₅SO₂C₂F₅ (~0.95 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 111 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 12 g/min at 275°C (estimated residence time 0.96 min) and 96.5 MPa for 150 minutes. After vacuum pump drying at room temperature, this gave 47 g of poly (HFP/TFE) for a productivity of 1.9 kg/L/hr. At 1 g of polymer per 5 ml of FC-75, an extremely viscous solution or near gel was obtained at room temperature. Fluorine NMR in the melt at 340°C found 45 wt % HFP/55 wt % TFE with 4.2% of the HFP methines as triads. GPC in FC-75 at 80°C found Mw = 892,000, Mn = 187,000, Mv = 776,000. Inherent viscosity in FC-75 at 25°C was 0.931. Roughly 58 g of polymer were made per gram of C₂F₅SO₂C₂F₅ initiator.

B. Initiation at 350°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml C₂F₅SO₂C₂F₅ (~0.95 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 112 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 12 g/min at 350°C (estimated residence time 0.96 min) and 96.5 MPa for 135 minutes. After vacuum pump drying at room temperature, this gave 97.6 g of poly (HFP/TFE) for a productivity of 4.3 kg/L/hr. One gram of polymer gave an attractive, clear solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 55 wt % HFP/45 wt % TFE. GPC in FC-75 at 80°C found Mw = 374,000, Mn = 152,000, Mv = 326,000. Inherent viscosity in FC-75 at 25°C was 0.408. Roughly 130 g of polymer were made per gram of C₂F₅SO₂C₂F₅ initiator.

C. Initiation at 400°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 1.03 g C₂F₅SO₂C₂F₅ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 151 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at ~13-26 g/min at 400°C (estimated residence time ~0.5 to 1 min) and 96.5 MPa for 85 minutes. Vacuum pump drying first at room temperature and then for four hours at 150°C gave 190 g of poly (HFP/TFE) for a productivity of 15 kg/L/hr. Dissolving 1 g in 5 ml of FC-75 at room temperature gave a clear

viscous solution, the most attractive solution of any of the 400°C samples. Fluorine NMR in the melt at 320°C found 58 wt % HFP/42 wt % TFE. GPC in FC-75 at 80°C found $M_w = 307,000$, $M_n = 111,000$, $M_v = 274,000$. Approximately 90 to 180 g of polymer were made per gram of $C_2F_5SO_2C_2F_5$ initiator.

EXAMPLE 74

n-Perfluorohexyl Iodide Initiation

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.5 ml n-perfluorohexyl iodide dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 113 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 9 g/min at 350°C (estimated residence time 1.3 min) and 96.5 MPa for 90 minutes. After vacuum pump drying at room temperature, this gave 39.6 g of poly (HFP/TFE) for a productivity of 2.6 kg/L/hr. One gram of polymer gave a hazy solution with a trace of particulates in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 56 wt % HFP/44 wt % TFE with 5% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 472,000$, $M_n = 119,000$, $M_v = 401,000$. Inherent viscosity in FC-75 at 25°C was 0.254. A NMR sample heated to 340°C turned dark purple indicating the incorporation of iodine into the polymer although no iodine color was detected in a melt index sample heated only to 200°C (melt index_{200°C, 5 kg} = 4 g/min). Roughly 100 g of polymer were made per gram of initiator.

EXAMPLE 75

2-Iodoheptafluoropropane Initiation

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.7 g 2-iodoheptafluoropropane dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 114 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at ~13 to 26 g/min at 350°C (estimated residence time ~ 0.5 to 1.0 min) and 96.5 MPa for 90 minutes. After vacuum pump drying at room temperature, this gave 102.8 g of poly (HFP/TFE) for a productivity of 6.8 kg/L/hr. The polymer was largely soluble in FC-75, 1 g in 5 ml FC-75 giving a hazy solution with residual flocculent solid at room temperature. Fluorine NMR in the melt at 340°C found 56 wt % HFP/44 wt % TFE. GPC in FC-75 at 80°C found $M_w = 157,000$, $M_n = 48,400$, $M_v = 135,000$. Roughly 130 to 270 g of polymer were formed per gram of 2-iodoheptafluoropropane initiator.

EXAMPLE 76**1,6-Diodododecafluorohexane Initiation**

A. $1X I(CF_2)_6I$: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 1.28 g 1,6-diiodododecafluorohexane dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 224 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 12.5 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 238 minutes. After vacuum pump drying at room temperature, this gave 180 g of poly (HFP/TFE) for a productivity of 4.5 kg/L/hr. One gram of polymer gave a solution with trace flocculent solids in 5 ml FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 59 wt % HFP/41 wt % TFE, the polymer sample turning pink with heating to 320°C. GPC in FC-75 at 80°C found $M_w = 221,000$, $M_n = 76,500$, $M_v = 190,000$. Roughly 200 g of polymer were formed per gram of 1,6-diiodododecafluorohexane initiator.

B. $10X I(CF_2)_6I$: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, 12.8 g 1,6-diiodododecafluorohexane was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 222 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 36.5 g/min at 350°C (estimated residence time 0.3 min) and 96.5 MPa for 105 minutes. Vacuum drying at room temperature gave 134 g of poly (HFP/TFE) for a productivity of 7.6 kg/L/hr. The polymer was soluble in FC-75, 1 g in 5 ml FC-75 giving a hazy solution with residual flocculent solid at room temperature. Fluorine NMR in the melt at 320°C found 47 wt % HFP/53 wt % TFE, the polymer sample turning deep purple with heating to 320°C. GPC in FC-75 at 80°C found $M_w = 94,800$, $M_n = 20,300$, $M_v = 66,700$. Roughly 11 g of polymer were formed per gram of 1,6-diiodododecafluorohexane initiator.

EXAMPLE 77 **$(C_4F_9)_2NF$ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.5 ml $(C_4F_9)_2NF$ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to 96.5 MPa reservoir 2 prior to the start of the run. A mix of this initiator with 114 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 115 minutes. After vacuum pump drying at room temperature, this gave 80.2 g of poly (HFP/TFE) for a productivity of 4.2 kg/L/hr. One gram of polymer gave a hazy solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 57 wt % HFP/43 wt

% TFE with 8.0% of the HFP methines as triads. GPC in FC-75 found $M_w = 426,000$, $M_n = 187,000$, $M_v = 378,000$. Inherent viscosity in FC-75 at 25°C was 0.380. Roughly 150 g of polymer were made per gram of $(C_4F_9)_2NF$ initiator.

When the polymer sample prepared here was heated at 10°C/min under N_2 , about 7% weight loss occurred between 50 and 130°C. Weight then stayed steady up until 320°C, at which point another ~10% weight loss occurred between ~320 and 420°C and finally ~70% by 500°C, the processes between 320 and 500°C presumably reflecting breaking of the polymer backbone. This onset of backbone degradation at 320°C is one of the reasons we are surprised that attractive high MW polymer can be made up to at least 400°C. The volatiles lost between 50 and 130°C were identified as largely perfluoromethylcyclobutane by infrared comparison to a genuine sample. If one wishes, virtually all of the perfluoromethylcyclobutane can be removed from a ~1:1 HFP copolymer sample by heating for several hours at ~150°C in a vacuum oven. The amount of perfluoromethylcyclobutane retained by polymer samples will reflect polymerization conditions (to what extent polymerization conditions favor the cycloaddition of TFE to HFP as a side reaction) as well as the conditions under which the polymer sample is collected (pressure, temperature, etc.). Once in the polymer sample, perfluoromethylcyclobutane is retained quite tightly. For many purposes, however, perfluoromethylcyclobutane can be considered an innocuous inert.

EXAMPLE 78

NF_3 Initiation

A. About 12:1 HFP: TFE, 1X NF_3 : The 10 cc shaken autoclave was set up as in Example 1. The 25 ml loop (1) off the feed line to reservoir (2) was pressured to 345 kPa (gauge) with nitrogen trifluoride at ambient temperature. A mix of this initiator with 218 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 13 g/min at 350°C (estimated residence time 0.9 min) and 96.5 MPa for 288 minutes. After vacuum pump drying at room temperature, this gave ~302 g of poly (HFP/TFE) for a productivity of ~6 kg/L/hr. One gram of polymer gave a solution with trace haze in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 58 wt % HFP/42 wt % TFE with 8% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 235,000$, $M_n = 74,200$, $M_v = 198,000$. Inherent viscosity in FC-75 at 25°C was 0.274. Roughly 1030 g of polymer were made per gram of NF_3 initiator.

B. About 12:1 HFP: TFE, 9X NF_3 : The polymerization above was repeated increasing the concentration of NF_3 initiator ~9 times while keeping other variables roughly the same. The 10 cc shaken autoclave was set up as in

Example 1. The 25 ml loop (1) off the feed line to reservoir (2) was pressured to 3.13 MPa (gauge) with nitrogen trifluoride at ambient temperature. A mix of this initiator with 228 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 11 to 22 g/min at 350°C (estimated residence time ~0.5 to 1.1 min) and 96.5 MPa for 315 minutes. After vacuum pump drying at room temperature, this gave 384 g of poly(HFP/TFE) for a productivity of ~7.3 kg/L/hr. One gram of polymer gave a clear solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 56 wt % HFP/44 wt % TFE with 10% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 212,000$, $M_n = 81,000$, $M_v = 182,000$. Inherent viscosity in FC-75 at 25°C was 0.181. Approximately 100 to 200 g of polymer were made per gram of NF_3 initiator.

C. About 16:1 HFP: TFE, 2X NF_3 : The 10 cc shaken autoclave was set up as in Example 1. The 25 ml loop (1) off the feed line to reservoir (2) was pressured to 758 kPa (gauge) with nitrogen trifluoride at ambient temperature. A mix of this initiator with 169 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 13 g/min at 350°C (estimated residence time 0.9 min) and 96.5 MPa for 252 minutes. After vacuum pump drying at room temperature, this gave ~215 g of poly (HFP/TFE) for a productivity of ~5 kg/L/hr. One gram of polymer gave a clear solution in 5 ml FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 58 wt % HFP/42 wt % TFE with 9% of the HFP methines as triads. Inherent viscosity in FC-75 at 25°C was 0.216. Roughly 440 grams of polymer were made per gram of initiator.

D. About 24:1 HFP: TFE, 2X NF_3 : The 10 cc shaken autoclave was set up as in Example 1. The 25 ml loop (1) off the feed line to reservoir (2) was pressured to 758 kPa (gauge) with nitrogen trifluoride at ambient temperature. A mix of this initiator with 112 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 12 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 300 minutes. Vacuum pump drying at room temperature and then overnight under vacuum at 150°C gave 140 g of poly (HFP/TFE) for a productivity of ~3 kg/L/hr. One gram of polymer gave a clear solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 62 wt % HFP/38 wt % TFE with 7% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 128,000$, $M_n = 32,800$, $M_v = 105,000$. Inherent viscosity in FC-75 at 25°C was 0.187. Roughly 260 g of polymer were made per gram of NF_3 initiator.

EXAMPLE 79

NF_3 Initiation

The 10 cc shaken autoclave was set up as in Example 1. The 25 ml loop (1) off the feed line to reservoir (2) was pressured to 345 kPa (gauge) with

nitrogen trifluoride at ambient temperature. A mix of this initiator with 154 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 10 g/min at 400°C (estimated residence time 1.2 min) and 96.5 MPa for 55 minutes. Vacuum pump drying at room temperature and then for 4 hours at 150°C gave 53 g of poly (HFP/TFE) for a productivity of 4.8 kg/L/hr. One gram polymer was soluble in 5 ml of FC-75 at room temperature with residual haze. Fluorine NMR in the melt at 320°C found 53 wt % HFP/47 wt % TFE with 4% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 173,000$, $M_n = 47,300$, $M_v = 138,000$. Roughly 620 g of polymer were made per gram of NF_3 initiator.

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EXAMPLE 80 **$C_4F_9SSC_4F_9$ Initiation**

A. At 350°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.5 ml $C_4F_9SSC_4F_9$ dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 113 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 150 minutes. After vacuum pump drying at room temperature, this gave 50.23 g of poly (HFP/TFE) for a productivity of 2.0 kg/L/hr. Consistent with its high molecular weight, 1 gram of polymer gave an extremely viscous, partial solution in 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 340°C found 50 wt % HFP/50 wt % TFE with 14.0% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 1,108,000$, $M_n = 238,000$, $M_v = 976,000$. Inherent viscosity in FC-75 at 25°C was 0.946. Roughly 70 g of polymer were made per gram of $C_4F_9SSC_4F_9$ initiator.

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B. At 400°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.5 ml $C_4F_9SSC_4F_9$ (0.89 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 151 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at ~12.7 g/min at 400°C (estimated residence time ~1.0 min) and 96.5 MPa for 85 minutes. After vacuum pump drying at room temperature and then for 4 hours under vacuum at 150°C, 185.9 g of poly (HFP/TFE) were obtained for a productivity of 13.0 kg/L/hr. Mixing 1 g of polymer with 5 ml FC-75 at room temperature gave a viscous solution with residual insolubles. Fluorine NMR in the melt at 320°C found 54 wt % HFP/46 wt % TFE. GPC in FC-75 at 80°C found $M_w = 361,000$, $M_n = 113,000$, $M_v = 306,000$. Roughly 210 g of polymer were made per gram of $C_4F_9SSC_4F_9$ initiator.

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EXAMPLE 81**(C₄F₉)₂NSCF₃ Initiation**

The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml (C₄F₉)₂NSCF₃ (0.92 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 80 g of TFE and 2200 g of HFP was run through the 10 ml agitated reactor at ~11 g/min at 350°C (estimated residence time 1.1 min) and 96.5 MPa for 105 minutes. Vacuum pump drying at room temperature and then for 4 hours at 150°C gave 97 g of poly (HFP/TFE) for a productivity of 5.5 kg/L/hr. One gram of polymer gave a viscous solution with residual insolubles when mixed with 5 ml of FC-75 at room temperature. Fluorine NMR in the melt at 320°C found 55 wt % HFP/45 wt % TFE. GPC in FC-75 at 80°C found Mw = 391,000, Mn = 116,000, Mv = 332,000. Roughly 210 g of polymer were made per gram of (C₄F₉)₂NSCF₃ initiator.

EXAMPLE 82**(C₄F₉)₃N Initiation**

A. At 350°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml (C₄F₉)₃N (0.94 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 117 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 117 minutes. After vacuum pump drying at room temperature, this gave 25 g of poly (HFP/TFE) for a productivity of 1.3 kg/L/hr. The polymer gave an extremely viscous solution or gel in FC-75. GPC in FC-75 at 80°C found Mw = 1,238,000, Mn = 153,000, Mv = 1,087,000. Inherent viscosity in FC-75 at 25°C was 1.375. Roughly 26 g of polymer were made per gram of (C₄F₉)₃N initiator.

B. At 400°C: The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF₃ as initiator, a solution of 0.5 ml (C₄F₉)₃N (0.94 g) dissolved in 2.0 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 157 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 13 g/min at 400°C (estimated residence time 0.9 min) and 96.5 MPa for 124 minutes. After vacuum pump drying at room temperature and then for ~15 hours under vacuum at 150°C, 120.0 g of poly (HFP/TFE) were obtained for a productivity of 5.8 kg/L/hr. Mixing 1 g of polymer with 5 ml of FC-75 at room temperature gave a solution with residual insolubles. Fluorine NMR in the melt at 320°C found 55 wt % HFP/45 wt % TFE. GPC in FC-75 at 80°C found Mw = 289,000, Mn =

78,300, $M_v = 238,000$. Roughly 130 g of polymer were made per gram of $(C_4F_9)_3N$ initiator.

EXAMPLE 83

$(C_4F_9)_2NF$ Initiation

5 The 10 cc shaken autoclave was set up as in Example 1. Instead of using NF_3 as initiator, a solution of 0.8 ml $(C_4F_9)_2NF$ (~1.4 g) dissolved in 5 ml of HFP cyclic dimer (perfluorodimethylcyclobutane) was introduced to reservoir 2 prior to the start of the run. A mix of this initiator with 223 g of TFE and 4000 g of HFP was run through the 10 ml agitated reactor at 12 g/min at 275°C (estimated
10 residence time 1.1 min) and 96.5 MPa for 315 minutes. After vacuum pump drying at room temperature, this gave 146 g of poly (HFP/TFE) for a productivity of 2.8 kg/L/hr. At room temperature 1 g of polymer dissolved in 5 ml of FC-75. Fluorine NMR in the melt at 340°C found 47 wt % HFP/53 wt % TFE with 7.4% of the HFP methines as triads. GPC in FC-75 at 80°C found $M_w = 603,000$, $M_n =$
15 226,000, $M_v = 546,000$. Inherent viscosity in FC-75 at 25°C was 0.679. Roughly 110 g of polymer were made per gram of $(C_4F_9)_2NF$ initiator.

EXAMPLE 84

NO ADDED INITIATOR

A. At 350°C: The 10 cc shaken autoclave was set up as in Example 1. No
20 initiator at all was added. A mix of 113 g of TFE and 2000 g of HFP was run through the 10 ml agitated reactor at 11 g/min at 350°C (estimated residence time 1.0 min) and 96.5 MPa for 115 minutes. After vacuum pump drying at room temperature, this gave 17.2 g of poly (HFP/TFE) for a productivity of 0.90 kg/L/hr. Rolling 1 g of polymer with 5 ml of FC-75 at room temperature
25 gave a hazy viscous solution. Fluorine NMR in the melt at 340°C found 57 wt % HFP/43 wt % TFE. GPC in FC-75 at 80°C found $M_w = 451,000$, $M_n = 147,000$, $M_v = 397,000$.

B. At 400°C: The 10 cc shaken autoclave was set up as in Example 1. No initiator at all was added. A mix of 154 g of TFE and 2000 g of HFP was run
30 through the 10 ml agitated reactor at 12 g/min at 400°C (estimated residence time 1.0 min) and 96.5 MPa for 110 minutes. After vacuum pump drying first at room temperature and then for four hours at 150°C, 77.9 g of poly (HFP/TFE) were obtained for a productivity of 4.2 kg/L/hr. Rolling 1 g of polymer with 5 ml of FC-75 at room temperature gave a hazy solution. Fluorine NMR in the melt at
35 320°C found 57 wt % HFP/43 wt % TFE. GPC in FC-75 at 80°C found $M_w = 262,000$, $M_n = 69,900$, $M_v = 208,000$.

EXAMPLE 85**TFE/HFP Copolymerization in a Well Stirred Reactor**

Three separate feed streams were converted to gases and metered into a mixing vessel typically at 200-380 kPa. The mixture was then compressed in two stages to goal pressures. The compressed super-critical fluid was fed to a preheater, held at 175 to 200°C in these experiments, and then into a stainless steel well-mixed reactor of 100 ml volume provided with a mechanical stirrer running at 1100 rpm. The design of this feed system assures that the flows are uniform and well controlled, since they are all handled as gases and compressed together.

From the reactor the polymer solution flows through a reducing valve, which was also used to control reactor pressure at 96.5 MPa, and thence into an enclosed collection vessel at 156 kPa where the unreacted monomers are allowed to evaporate. The evaporated monomers are condensed and collected in a separate system. Product was removed from the collection vessel at the end of the run.

Typical example conditions are shown in the following table which also shows the properties of the resulting product.

	<u>Units</u>	<u>Run A</u>	<u>Run B</u>	<u>Run C</u>
Feed 1: (100% HFP)	Kg/hr	4.7	5.03	3.84
Feed 2: Wt. % NF ₃ in HFP	Wt. %	1.32	2.49	0.87
Rate	Kg/hr	0.045	0.049	0.022
Feed 3: (100% TFE)	Kg/hr	0.21	0.20	0.26
Mixer Pressure	kPa	255	276	200
Preheater Temperature	°C	175	200	190
Reactor Temperature	°C	267	275	284
Polymerization Reactor Pressure	MPa	96.5	96.5	41.3-55.1
Production rate	gm/hr	168	196	248
Product properties:				
Wt percent HFP	%	54.7	58.9	50.7
Molecular weight Mn		113,000	71,600	140,000
Molecular weight Mw		325,000	170,000	371,000
Mw/Mn		2.87	2.37	2.64
Calculated TFE conversion	%	36.2	40.3	43.6

EXAMPLE 86**CF₃CF₂CF₂C(CF₃)₂NF₂**

A: A 2 liter r.b. flask with a stirring bar was charged with 75 g of dry, ball-milled KF in a glove box. The flask was transferred to a hood, swept with nitrogen, and 1 liter of 4A molecular sieve dried dimethylformamide added with

stirring. The contents of the flask were chilled to -12°C and the addition of phenyldiazonium tetrafluoroborate was begun. Soon into the addition the contents of the flask were further chilled to -37°C and phenyldiazonium tetrafluoroborate addition continued, a total of 282.9 g being added.

5 With the temperature at -35 to -40°C , 325.3 g of $(\text{CF}_3)_2\text{C}=\text{CFCF}_2\text{CF}_3$ were added in a trickle, then 27.2 g of dry KF, and finally another 119.6 g of $(\text{CF}_3)_2\text{C}=\text{CFCF}_2\text{CF}_3$. As the last of the $(\text{CF}_3)_2\text{C}=\text{CFCF}_2\text{CF}_3$ was run in, temperature increased to -31°C and foaming increased. The reaction mixture was chilled to and held at -38°C for an hour. Temperature was allowed then to
10 gradually rise to room temperature. The reaction mixture was stirred overnight at room temperature under nitrogen. The solids were filtered off and washed with ether. The filtrate was taken up in about 2 liters of ether, washed with water, 5X with 5% NaOH, 4X with 5% HCl, each aqueous wash back-washed with 1 liter of ether. The ether layer was washed with saturated sodium chloride, dried over
15 CaCl_2 , and concentrated on a rotary evaporator. This gave 283.6 g of crude dark red oil. This oil was dissolved in 500 g of trifluoroacetic acid. Reduction was quite slow taking the addition of 54 g amalgamated zinc, 44 g of amalgamated zinc four days later, 300 g trifluoroacetic acid and 40 g amalgamated zinc about 23 days later, and then an additional 15 day wait. The reaction mixture was worked up by
20 adding 1 liter of distilled water and steam distilling directly out of the flask. Steam distillation accompanied by foaming gave 152.7 g of crude $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{NH}_2$ using a Dean-Stark trap for collection. Three such batches (totaling ~360 g) ranging in GC purity from 79 to 96% were combined and added slowly to 50 ml Et_2NH mixed with 100 ml 40% aqueous KOH (exotherm,
25 slow addition). After stirring overnight, the reaction mixture was poured into water, washed several times with 5% HCl, and dried. Attempted distillation at this point gave fumes and discoloration and was discontinued. The reaction mixture was added to a solution made by dissolving 133 g of 85% KOH in 150 ml water and 500 ml ethanol. This mixture was stirred overnight and then refluxed over the
30 next night. Water was added to nearly fill the 2 liter reaction flask and then the contents steam distilled. This distillate was washed with water and the lower layer, 284.8 g, then dried over CaCl_2 . The fluorine NMR was very clean while GC showed a short retention time impurity with an area of 8.7%. This $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{NH}_2$ was used in step B below.

35 B: A 60 ml Teflon® bottle was loaded with 9.62 g of $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{NH}_2$. Over a period of 4.55 hr, 1726 ml of F_2 gas was passed into the bottle at atmospheric pressure and room temperature while stirring the contents gently. The reaction mixture was let stand overnight at room temperature. A pipette was used to withdraw 8.33 g of light yellow fluid from the

Teflon® bottle. Fluorine NMR was consistent with quantitative conversion to the desired $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{NF}_2$: +36.0 ppm (1.9 F), -62.3 ppm (6.0 F), -81.0 ppm (3.05 F), -109.2 ppm (1.9 F), -123.3 ppm (2.0 F). No other adsorptions were visible in the fluorine NMR, yield 78%. In a similar, larger scale run, a center cut of colorless distillate was taken off a little NaF ($\text{bp}_{760} = 84-88^\circ\text{C}$).

Calc. for $\text{C}_6\text{F}_{13}\text{NF}_2$:	19.42C	76.80F	3.78N
Found:	19.35C	76.93F	3.71N

10

EXAMPLE 87 $(\text{C}_4\text{F}_9)_2\text{NSCF}_3$

A 100 ml flask was charged with $\text{C}_4\text{F}_9\text{N}=\text{CFC}_3\text{F}_7$ (5.0 g 11.5 mmol), CsF (2.3 g, 15 mmol), and 10 ml of diethyl ether under a N_2 atmosphere. After stirring for 3 hours at room temperature, the mixture was cooled to -5°C by an ice-water bath and CF_3SCl (excess) added via a dry ice-acetone condenser until a slight yellow color was observed in the mixture. The resulting mixture was stirred at room temperature for one day. Then the mixture was filtered, the filtrate partially distilled to remove ether, and the residue bulb-to-bulb distilled at reduced pressure to afford 4.8 g (75%) of colorless liquid, a small amount of which when heated in a melting point capillary showed the initiation of boiling at -145°C . ^{19}F NMR was consistent with the desired product $(\text{C}_4\text{F}_9)_2\text{NSCF}_3$: -50.1 (m, 3F), -81.4 (t, J = 10 Hz, 6F), -86.0 (AB q, J = 233 Hz, 4F), -121.0 (AB q, J = 290 Hz, 4F), -126.9 (t, J = 15 Hz, 4F).

EXAMPLES 88-118

25

Other Monomers in High Temperature PolymerizationExperimental

New monomer combinations are described in Examples 88-118 below. Polymerizations were run in a semicontinuous fashion using the equipment and general methods described in Example 1. Weights of TFE added to the mixing reservoir were calculated the same way as in Examples 66 and 84. In cases where an NMR analysis of polymer composition was not available, elemental analysis was often performed assuming a 1:1 HFP:TFE molar ratio for purposes of calculation. At high levels of incorporation and high temperatures, those termonomers with chain transferring groups often gave greases and oils rather than solid polymer. This includes methyl vinyl ether, propylene, isobutylene, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCF}=\text{CF}_2$.

Compositions for many of the TFE/HFP copolymers were determined from ^{19}F spectra taken either on polymer melts at 300 to 340°C or on solutions in hexafluorobenzene at 80°C . Integration of the CF peaks at -174 ppm to -185 ppm

was used to determine HFP content, and the CF_2 absorptions at -100 ppm to -125 ppm, corrected for comonomer contributions, for the TFE content. The termonomer content was determined from the integrated intensities of the relevant signals: $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$ (Example 97) from the signal at -82.5 ppm, $\text{CF}_2=\text{CFOCF}_2(\text{CF}_3)\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ and $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (Examples 94A and 93) from the signal at +46.2 ppm, $\text{CH}_2=\text{CHOCOCF}_3$ (Example 96) from the signal at -77.5 ppm, $\text{CF}_2=\text{CFOCF}_2(\text{CF}_3)\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ in the melt (Example 94B) using various -OCF absorptions around -75 to -83 and -136 to -140 ppm, $\text{CF}_2=\text{CFCF}_2\text{CN}$ (Example 92) from the signal at -107 ppm, CTFE (Example 91A) from the signals at -129 ppm -134 ppm, $\text{CF}_3\text{CH}=\text{CH}_2$ from the CF_3 CH signal at -67 ppm, perfluorocyclobutene by difference between the observed excess CF's around -175 to -185 ppm compared to what expected from HFP alone (Example 106), perfluorocyclopentene (Example 107) same as the perfluorocyclobutene, $\text{CF}_2=\text{C}(\text{CF}_3)\text{COF}$ from the -COF resonance at about 20 ppm (Example 109), trifluoroethylene from the -CFH- resonance at -199 ppm (Example 110), perfluoro-2-methylene-4-methyl-1,3-dioxolane from the resonances for the -OCF₂ and the -CF₃ at -80 to -82 ppm (Example 111).

Composition of polymers containing VF2 as the third monomer (Example 88 to 90) were determined from both the ^{19}F spectrum and a ^1H spectrum taken on a sample of the polymer into which an internal standard, containing both fluorine and protons, had been added. The VF2 ^1H signal at 2.2 ppm was ratioed to the internal standard signals, converted into an absolute amount of VF2 which was subtracted from a weighed amount of the polymer to give the amount of polymer which was not VF2. Polymers containing both TFE and HFP along with VF2 determined the TFE and HFP in the way mentioned above.

The composition of polymers containing ethylene as a third monomer (Example 98) were determined from both the ^{19}F and ^{13}C spectra taken on solutions in hexafluorobenzene. The ^{19}F spectrum was used to determine the ratio of the HFP to TFE. The ^{13}C spectrum was used to determine the integrated intensities of the CF_2 signals at 106 ppm - 126 ppm, the CF signals at 91 ppm - 99 ppm, and the CH_2 signals at 20 ppm - 28 ppm.

The composition of the HFP/TFE/ $\text{CF}_3\text{CF}=\text{CH}_2$ terpolymer was determined by ^{13}C NMF using the CH_2 carbon from 30 and 32 ppm for $\text{CF}_3\text{CF}=\text{CH}_2$, the CF carbon at 98 to 100 ppm for $\text{CF}_3\text{CF}=\text{CF}_2$ after subtraction of the CF contributed by tetrafluoropropene, and the CF_2 carbon from 110 to 132 ppm for TFE after subtraction of CF_3 and CF_2 carbons contributed by hexafluoropropene and tetrafluoropropene (Example 101).

EXAMPLE 88**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/VF2**

The same set up was used as in Example 1. A mixture of 4000 g of HFP,
 5 220 g TFE, 3 g vinylidene fluoride, and about 1.2 g of NF_3 was made in 96.5 MPa
 reservoir (2). About 3548 g of this mixture were run through the 10 ml shaken
 autoclave at 250°C and 96.5 MPa over a 275 minute period. Drying the product
 under vacuum gave 177 g of white polymer. Analysis results are gathered below.

> 1 g/5 ml of FC-75, clear solution at room temperature
 10 $M_w = 299,000$ by GPC in FC-75 at 80°C
 $M_n = 111,000$ by GPC in FC-75 at 80°C
 Inherent Viscosity in FC-75 at 25°C = 0.384
 Melt index_{185°C, 5 kg} = 0.7 g/min
 Tg = 28°C (second heat) by DSC @10°C/min under N_2
 15 Tm, none detected by DSC @10°C/min, N_2 , second heat
 10% weight loss temperature 420°C @10°C/min under N_2
 ~2 mole % VF2 by ^{19}F NMR in melt at 320°C
 ~39 mole % HFP by ^{19}F NMR in melt at 320°C
 ~59 mole % TFE by ^{19}F NMR in melt at 320°C
 20 Productivity 3.8 kg/L/hr (32 lbs/gal/hr)

EXAMPLE 89**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/VF2**

The same set up was used as in Example 1. A mixture of 4000 g of HFP,
 25 164 g TFE, 40 g vinylidene fluoride, and about 1.2 g of NF_3 was made in
 96.5 MPa reservoir (2). About 3302 g of this mixture were run through the 10 ml
 shaken autoclave at 275°C and 96.5 MPa over a 185 minute period. Drying the
 product under vacuum gave 180 g of white polymer. Analysis results are gathered
 below.

30 Little or partial solubility at 1 g/5 ml FC-75, Freon® 113, or
 acetone at r.t.
 $M_w = 122,000$ by GPC in FC-75 at 80°C
 $M_n = 38,300$ by GPC in FC-75 at 80°C
 Inherent Viscosity in FC-75 at 25°C = 0.247 (cloudy solution)
 35 Melt index_{185°C, 5 kg} = 1 g/min
 Tg = 2°C (second heat) by DSC @10°C/min under N_2
 Tm, none detected by DSC @10°C/min, N_2 , second heat
 10% weight loss temperature 410°C @10°C/min under N_2

~29 mole % VF₂ by ¹⁹F NMR in melt at 300°C
 ~39 mole % HFP by ¹⁹F NMR in melt at 300°C
 ~32 mole % TFE by ¹⁹F NMR in melt at 300°C
 Productivity 5.8 kg/L/hr (49 lbs/gal/hr)

5

EXAMPLE 90**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/VF₂**

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 80 g vinylidene fluoride, and about 0.6 g of NF₃ was made in 96.5 MPa reservoir (2). About 1656 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 139 minute period. Drying the product under vacuum gave 105 g of white polymer. Analysis results are gathered below.

0.1 g/1 ml solubility in Freon® 113 or acetone at r.t.
 Inherent Viscosity in Freon® 113 at 25°C = 0.044
 T_g = -5°C (second heat) by DSC @10°C/min under N₂
 T_m, none detected by DSC @10°C/min. N₂, second heat
 10% weight loss temperature 190°C @10°C/min under N₂
 ~59 mole % VF₂ by ¹⁹F NMR in melt at 300°C
 ~41 mole % HFP by ¹⁹F NMR in melt at 300°C
 Productivity 4.5 kg/L/hr (38 lbs/gal/hr)

20

EXAMPLE 91**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/CTFE**

A. ~124:9.2:1 HFP:TFE:CTFE: The same set up was used as in Example 1. A mixture of 4000 g of HFP, 197 g TFE, 25 g chlorotrifluoroethylene, and about 1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 4057 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 266 minute period. Drying the product under vacuum gave 120 g of white polymer. Analysis results are gathered below.

1 g/5 ml soluble in FC-75 at r.t. with a trace of flocculent residue
 M_w = 171,000 by GPC in FC-75 at 80°C
 M_n = 65,300 by GPC in FC-75 at 80°C
 T_g = 30°C (second heat) by DSC @10°C/min under N₂
 T_m, none detected by DSC @10°C/min. N₂, second heat
 10% weight loss temperature. 410°C @ 10°C/min under N₂
 2.9 mole % CTFE by ¹⁹F NMR in melt at 320°C
 40.6 mole % HFP by ¹⁹F NMR in melt at 320°C
 56.5 mole % TFE by ¹⁹F NMR in melt at 320°C

35

Productivity 2.7 kg/L/hr (22 lbs/gal/hr)

B. ~15:1.2:1 HFP:TFE:CTFE: The same set up was used as in Example 1.

A mixture of 2000 g of HFP, 108 g TFE, 100 g chlorotrifluoroethylene, and about 0.6 g of NF₃ was made in 96.5 MPa reservoir (2). About 1913 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 140 minute period. Drying the product under vacuum gave 107 g of white polymer. Analysis results are gathered below.

1 g/5 ml soluble in FC-75 at r.t., hazy flocculent residue

Mw = 39,100 by GPC in FC-75 at 80°C

Mn = 15,300 by GPC in FC-75 at 80°C

Melt index_{120°C, 5 kg} = 8 g/min

Tg = 26°C (second heat) by DSC @10°C/min under N₂

10% weight loss temperature, 390°C @ 10°C/min under N₂

Tm, none detected by DSC @10°C/min under N₂

19 mole % CTFE by ¹⁹F NMR in melt at 320°C

27 mole % HFP by ¹⁹F NMR in melt at 320°C

54 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 4.6 kg/L/hr (38 lbs/gal/hr)

EXAMPLE 92

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/NCCF₂CF=CF₂

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 114 g TFE, 68 g NCCF₂CF=CF₂, and about 1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1912 g of this mixture were run through the 10 ml shaken autoclave at 275°C and 96.5 MPa over a 175 minute period. Drying the product under vacuum gave 32 g of white polymer. Analysis results are gathered below.

1 g soluble 5 ml FC-75 at r.t. with a bit of residual flocculent solids

Mw = 58,900 by GPC in FC-75 at 80°C

Mn = 24,800 by GPC in FC-75 at 80°C

Inherent Viscosity in FC-75 at 25°C = 0.119

Melt index_{100°C, 5 kg} = 2.4 g/min

Tg = 25°C (second heat) by DSC @10°C/min under N₂

Tm, none detected by DSC @10°C/min. N₂, second heat

10% weight loss temperature, 410°C @ 10°C/min under N₂

~0.6 mole % NCCF₂CF=CF₂ by ¹⁹F NMR, hexafluorobenzene, 80°C

~37 mole % HFP by ¹⁹F NMR, hexafluorobenzene solution, 80°C

~62 mole % TFE by ¹⁹F NMR, hexafluorobenzene solution, 80°C

Productivity 1.1 kg/L/hr (9 lbs/gal/hr)

EXAMPLE 93

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/FSO₂CF₂CF₂OCF₂CF=CF₂

5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 114 g TFE, 84 g FSO₂CF₂CF₂OCF₂CF=CF₂, and about 1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1125 g of this mixture were run through the 10 ml shaken autoclave at 275°C and 96.5 MPa over a 115 minute period. Drying the product under vacuum gave 61.5 g of white polymer. Of this a 10.9 g sample was
10 dried for another 4 hours at 150°C in a vacuum oven, giving 10.4 g fused solid with the following analyses. Analysis results are gathered below.

1 g soluble 5 ml FC-75 at r.t. with a bit of residual flocculent solids
Mw = 142,000 by GPC in FC-75 at 80°C
Mn = 55,800 by GPC in FC-75 at 80°C
15 Inherent Viscosity in FC-75 at 25°C = 0.190
Melt index_{200°C, 5 kg} = 4 g/min
Tg = 26°C (second heat) by DSC @10°C/min under N₂
Tm, none detected by DSC @10°C/min. N₂, second heat
10% weight loss temperature 430°C @10°C/min under N₂
20 ~0.25 mole % FSO₂CF₂CF₂OCF₂CF=CF₂ by ¹⁹F NMR in melt at 150°C
~37 mole % HFP by ¹⁹F NMR in melt at 150°C
~63 mole % TFE by ¹⁹F NMR in melt at 150°C
Productivity 3.0 kg/L/hr (25 lbs/gal/hr)

25

EXAMPLE 94

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ (PSEPVE)

A. ~240:20:1 HFP:TFE:PSEPVE. The same set up was used as in Example 1. A mixture of 4000 g of HFP, 221 g TFE, 30 mL
30 FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, and about 1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1639 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 184 minute period. The polymer was dried under vacuum first at room temperature and then overnight at 150°C giving 62 g of fused sheet. Analysis results are gathered below.

35 1 g soluble 5 ml FC-75 at r.t. with a trace of haze
Mw = 77,600 by GPC in FC-75 at 80°C
Mn = 37,300 by GPC in FC-75 at 80°C
Inherent Viscosity in FC-75 at 25°C = 0.128

- T_g = 14°C (second heat) by DSC @10°C/min under N₂
 T_m, none detected by DSC @10°C/min, N₂, second heat
 10% weight loss temperature 380°C @10°C/min under N₂
 ~0.7 mole % FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ by ¹⁹F NMR in
 5 hexafluorobenzene solution at 80°C
 ~37 mole % HFP by ¹⁹F NMR in hexafluorobenzene solution at
 80°C
 ~61 mole % TFE by ¹⁹F NMR in hexafluorobenzene solution at
 80°C
 10 ~1% FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ as free monomer by
¹⁹F NMR in hexafluorobenzene solution at 80°C
 Productivity 2.0 kg/L/hr (17 lbs/gal/hr)

- B. ~~~240:30:1 HFP:TFE:PSEPVE~~. The same set up was used as in
 Example 1. A mixture of 2667 g of HFP, 224 g TFE, 33 g
 15 FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, and about 1.2 g of NF₃ was made in
 96.5 MPa reservoir (2). About 2527 g of this mixture were run through the 10 ml
 shaken autoclave at 250°C and 96.5 MPa over a 215 minute period. The polymer
 was dried under vacuum first at room temperature and then for 4 hours at 150°C
 giving 232.9 g. TGA found that about 5 wt % of PSEPVE was still retained by the
 20 polymer coming off at about 130-170°C. The remaining 221.7 g sample of polymer
 was further dried for 4 hours at 200°C in a vacuum oven, giving 200.3 g of flexible
 orange, clear polymer. Analysis results are gathered below.

- 1 g partially soluble in 5 ml FC-75 at r.t.
 Mw = 61,600 by GPC in FC-75 at 80°C
 25 Mn = 25,300 by GPC in FC-75 at 80°C
 T_g = 15°C (second heat) by DSC @10°C/min under N₂
 10% weight loss temperature 390°C @10°C/min under N₂
 T_m, none detected by DSC @10°C/min, N₂, second heat
 0.6 mole % FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ by ¹⁹F NMR
 30 320°C
 35.2 mole % HFP by ¹⁹F NMR in melt at 320°C
 64.2 mole % TFE by ¹⁹F NMR in melt at 320°C
 Productivity 5.9 kg/L/hr (49 lbs/gal/hr)

EXAMPLE 95

- 35 Continuous Polymerization in 10 ml Autoclave with Agitation
HFP/TFE/Perfluoro-2-Methyl-2,3-dihydro-1,4-dioxin (PMDD)

The same set up was used as in Example 1. A mixture of 1000 g of HFP, 62 g TFE, 24.7 g perfluoro-2-Methyl-2,3-dihydro-1,4-dioxin, and about 0.6 g of

NF₃ was made in 96.5 MPa reservoir (2). About 650 g of this mixture were run through the 10 ml shaken autoclave at 275°C and 96.5 MPa over a 54 minute period. The polymer was dried under vacuum at room temperature, 53.5 g.

- 5 1 g largely soluble 5 ml FC-75 at r.t. with a residue of flocculent solid
- Mw = 53,600 by GPC in FC-75 at 80°C
- Mn = 25,100 by GPC in FC-75 at 80°C
- Inherent Viscosity in FC-75 at 25°C = 0.092
- Tg = 30°C (second heat) by DSC @10°C/min under N₂
- 10 Tm, none detected by DSC @10°C/min, N₂, second heat
- ~0.5 mole % perfluoro(5-methyl-2,3-dihydro-1,4-dioxin) by ¹⁹F NMR in melt at 300°C
- ~45 mole % HFP by ¹⁹F NMR in melt at 300°C
- ~55 mole % TFE by ¹⁹F NMR in melt at 300°C
- 15 Productivity 5.9 kg/L/hr (49 lbs/gal/hr)

EXAMPLE 96

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CH₂=CHO(C=O)CF₃

- 20 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 113 g TFE, 10 ml (12 g) vinyl trifluoroacetate, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1739 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 152 minute period. Drying the product under vacuum gave 105.3 g of white polymer, a 10.32 g sample of which was dried further for 4 hours at 150°C under vacuum, giving 9.9 g of colorless polymer. Results for the oven dried 9.9 g sample are gathered below.

- 25 1 g/5 ml FC-75 at r.t., hazy solution, trace insolubles
- Mw = 78,900 by GPC in FC-75 at 80°C
- Mn = 23,500 by GPC in FC-75 at 80°C
- Melt index_{120°C, 5 kg} = 8 g/min
- 30 Tg = 26°C (second heat) by DSC @10°C/min under N₂
- 10% weight loss temperature 380°C @10°C/min under N₂
- Tm, none detected by DSC @10°C/min, N₂, second heat
- ~5 mole % CH₂=CHO(C=O)CF₃ by ¹⁹F NMR in melt
- ~41 mole % HFP by ¹⁹F NMR in melt
- 35 ~54 mole % TFE by ¹⁹F NMR in melt
- Productivity 4.0 kg/L/hr (33 lbs/gal/hr)

EXAMPLE 97**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/CH₂=CHCF₂CF₂CF₂CF₃**

The same set up was used as in Example 1. A mixture of 2000 g of HFP,
 5 114 g TFE, 10 ml (14.4 g) perfluorobutylethylene, and ~1.2 g of NF₃ was made in
 96.5 MPa reservoir (2). About 1777 g of this mixture were run through the 10 ml
 shaken autoclave at 250°C and 96.5 MPa over a 135 minute period. Drying the
 product under vacuum gave 51.8 g of white polymer, a 10.13 g sample of which
 was dried further for 4 hours at 150°C under vacuum, giving 8.75 g of colorless
 10 polymer. Analysis results for the oven dried 8.75 g sample are gathered below.

1 g/5 ml FC-75 at r.t., hazy solution, trace insolubles

Mw = 53,000 by GPC in FC-75 at 80°C

Mn = 22,700 by GPC in FC-75 at 80°C

Tg = 17°C (second heat) by DSC @10°C/min under N₂

15 10% weight loss temperature 390°C @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

4 mole % CF₃CF₂CF₂CF₂CH=CH₂ by ¹⁹F NMR in melt at 320°C

37 mole % HFP by ¹⁹F NMR in melt at 320°C

59 mole % TFE by ¹⁹F NMR in melt at 320°C

20 Productivity 2.0 kg/L/hr (17 lbs/gal/hr)

EXAMPLE 98**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/CH₂=CH₂**

The same set up was used as in Example 1. A mixture of 2000 g of HFP,
 25 113 g TFE, 8 g ethylene, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2).
 About 1533 g of this mixture were run through the 10 ml shaken autoclave at
 250°C and 96.5 MPa over a 143 minute period. Drying the product under vacuum
 gave 93.8 g of white polymer, a 10.78 g sample of which was dried further for
 4 hours at 150°C under vacuum, giving 10.45 g of colorless polymer. Results for
 30 the oven dried 10.45 g sample are gathered below.

1 g/5 ml FC-75 at r.t., hazy, low viscosity solution

Mw = 61,600 by GPC in FC-75 at 80°C

Mn = 19,000 by GPC in FC-75 at 80°C

Melt index_{120°C, 5 kg} = 2.7 g/min

35 Tg = 23°C (second heat) by DSC @10°C/min under N₂

10% weight loss temperature, 380°C @ 10°C/min under N₂

Tm, none detected by DSC @10°C/min under N₂

15.4 mole % ethylene by ¹³C NMR in solution

40.2 mole % HFP by ^{13}C NMR in solution
 44.4 mole % TFE by ^{13}C NMR in solution
 Productivity 3.8 kg/L/hr (32 lbs/gal/hr)

EXAMPLE 99

5 Continuous Polymerization in 10 ml Autoclave with Agitation
 HFP/TFE/ $\text{CH}_2=\text{CHCH}_3$

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 114 g TFE, 8 g propylene, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1616 g of this mixture were run through the 10 ml shaken autoclave at 10 250°C and 96.5 MPa over a 150 minute period. Drying the product for 4 hours under vacuum at 150°C gave 25.4 g of pale yellow grease/oil.

1 g/5 to 10 ml FC-75 at r.t., clear solution
 Mw = 9,350 by GPC in FC-75 at 80°C
 Mn = 4,220 by GPC in FC-75 at 80°C
 15 Tg = -23.7°C (second heat) by DSC @10°C/min under N_2
 Tm, none detected by DSC @10°C/min, N_2 , second heat
 TGA, 10°C/min., N_2 , 10% weight loss at ~150°C
 Productivity 1.0 kg/L/hr (8.4 lbs/gal/hr)
 Elemental Analysis, Found: 1.68% H, 1.68% H
 20 Calc.: * (TFE)~1.28x(HFP)~1.28x(C_3H_6)x 1.67% H
 * 1:1 HFP: TFE ratio assumed

EXAMPLE 100

25 Continuous Polymerization in 10 ml Autoclave with Agitation
 HFP/TFE/ $\text{CH}_2=\text{CHCF}_3$

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 105 g TFE, 10 g 3,3,3-trifluoropropene, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1855 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 160 minute period. Drying the product under vacuum for 4 hours at 150°C gave 98.8 g of a fused mass that hardened on 30 cooling.

1 g/5 to 10 ml FC-75 at r.t., clear solution
 Mw = 35,000 by GPC in FC-75 at 80°C
 Mn = 13,800 by GPC in FC-75 at 80°C
 35 Tg = 13°C (second heat) by DSC @10°C/min under N_2
 10% weight loss temperature 390°C @10°C/min under N_2
 Tm, none detected by DSC @10°C/min, N_2 , second heat
 7 mole % $\text{CF}_3\text{CH}=\text{CH}_2$ by ^{19}F NMR in melt at 320°C
 38 mole % HFP by ^{19}F NMR in melt at 320°C

55 mole % TFE by ^{19}F NMR in melt at 320°C
 Productivity 3.7 kg/L/hr (31 lbs/gal/hr)

EXAMPLE 101

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/ $\text{CH}_2=\text{CFCF}_3$

5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 112 g TFE, 10 g 2,3,3,3-tetrafluoropropene, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1652 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 151 minute period. Drying the
 10 product for 4 hours at 150°C under vacuum gave 74.8 g of colorless polymer.

1 g/5 ml FC-75 at r.t., clear solution

$M_w = 42,900$ by GPC in FC-75 at 80°C

$M_n = 18,600$ by GPC in FC-75 at 80°C

$T_g = 17^\circ\text{C}$ (second heat) by DSC @ $10^\circ\text{C}/\text{min}$ under N_2

15 10% weight loss temperature 380°C @ $10^\circ\text{C}/\text{min}$ under N_2

T_m , none detected by DSC @ $10^\circ\text{C}/\text{min}$, N_2 , second heat

8.6 mole % $\text{CF}_3\text{CF}=\text{CH}_2$ ^{13}C NMR in hexafluorobenzene @ 60°C

36.2 mole % HFP by ^{13}C NMR in hexafluorobenzene solution @ 60°C

20 55.2 mole % TFE by ^{13}C NMR in hexafluorobenzene solution @ 60°C

Productivity 3.0 kg/L/hr (25 lbs/gal/hr)

EXAMPLE 102

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/ $\text{CH}_2=\text{C}(\text{CH}_3)_2$

25 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 113 g TFE, 8 g isobutylene, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1616 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 150 minute period. Drying the product for 4 hours
 30 under vacuum at 150°C gave 34.8 g of yellow grease.

1 g/5 to 10 ml $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ at r.t., largely soluble

$M_w = 12,500$ by GPC in FC-75 at 80°C

$M_n = 4,690$ by GPC in FC-75 at 80°C

$T_g = -12.6^\circ\text{C}$ (second heat) by DSC @ $10^\circ\text{C}/\text{min}$ under N_2

35 TGA, $10^\circ\text{C}/\text{min}$, N_2 , 10% weight loss at $\sim 130^\circ\text{C}$

T_m , none detected by DSC @ $10^\circ\text{C}/\text{min}$, N_2 , second heat

Productivity 1.3 kg/L/hr (11 lbs/gal/hr)

Elemental Analysis, Found: 1.89% H, 1.78% H

Calc.:* (TFE)_{-1.52x}(HFP)_{1.52x}(C₄H₈)_x 1.84% H

* 1:1 HFP: TFE ratio assumed

EXAMPLE 103

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CH₃CH₂CH₂CH₂OCF=CF₂

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 111 g TFE, 10 g n-butyl trifluorovinyl ether, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1748 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 150 minute period. Drying the product for 4 hours under vacuum at 150°C gave 28.8 g of orange grease.

1 g/5 to 10 ml FC-75 at r.t., opalescent solution

Mw = 17,500 by GPC in FC-75 at 80°C

Mn = 6,890 by GPC in FC-75 at 80°C

Tg = -3°C (second heat) by DSC @10°C/min under N₂

TGA, 10°C/min., N₂, 10% weight loss at ~150°C

Tm, none detected by DSC @10°C/min, N₂, second heat

Productivity 1.1 kg/L/hr (9.6 lbs/gal/hr)

Elemental Analysis, Found: 0.62% H, 0.65% H

Calc.:* (TFE)_{-5x}(HFP)_{-5x}(C₆H₉F₃O)_x 0.64 %H

* 1:1 HFP: TFE ratio assumed

EXAMPLE 104

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CH₂=CHCF₂CF₂Br

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 114 g TFE, 14.5 g 4-bromo-3,3,4,4-tetrafluoro-1-butene, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1678 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 164 minute period. Drying the product under vacuum gave 86.7 g of off-white polymer, a 10.45 g sample of which was dried further for 4 hours at 150°C under vacuum, giving 8.9 g of colorless polymer. Results for the oven dried 8.9 g sample are gathered below.

1 g/5 ml FC-75 at r.t., clear solution

Mw = 20,300 by GPC in FC-75 at 80°C

Mn = 7,290 by GPC in FC-75 at 80°C

Tg = 10°C (second heat) by DSC @10°C/min under N₂

10% wt. loss in TGA @10°C/min under N₂: 320°C

Tm, none detected by DSC @10°C/min, N₂, second heat

Productivity 2.7 kg/L/hr (22 lbs/gal/hr)

Elemental Analysis, Found: 4.10% Br, 4.07% Br. Calc.:*

(TFE)_{-7.02x}(HFP)_{-7.02x}(C₄H₃F₄Br)_x 4.07% Br

1:1 HFP: TFE ratio and bromine only as part of original monomer assumed

EXAMPLE 105

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CH₂=CHOCH₃

5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 92 g TFE, 5 g methyl vinyl ether, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1512 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 130 minute period. Drying the product under vacuum gave 46.9 g of tacky yellow grease, a 13.44 g sample of which was dried further for 4 hours at 150°C under vacuum, giving 11.48 g of grease unchanged in appearance. Results for the oven dried 11.48 g sample are gathered below.

1 g/5 to 7 ml CF₃CFHCFHCF₂CF₃ at r.t., clear solution
 15 Mw = 7,940 by GPC in FC-75 at 80°C
 Mn = 4,650 by GPC in FC-75 at 80°C
 10% wt. loss in TGA @10°C/min under N₂: 200°C
 Productivity 1.4 kg/L/hr (12 lbs/gal/hr)
 Elemental Analysis, Found: 0.94 & 0.93% H
 20 Calc.: * (TFE)~2.4x(HFP)~2.4x(C₃H₆O)x 0.92 % H
 * 1:1 HFP: TFE ratio assumed

EXAMPLE 106

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/Perfluorocyclobutene

25 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 111 g TFE, 10 g perfluorocyclobutene, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1739 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 145 minute period. Drying the product for 4 hours under vacuum at 150°C gave 91.6 g of colorless polymer.

30 1 g/5 ml FC-75 at r.t., viscous hazy solution, some flocculent solids
 Mw = 213,000 by GPC in FC-75 at 80°C
 Mn = 78,600 by GPC in FC-75 at 80°C
 Melt index_{120°C, 15 kg} = 0.8 g/min
 Tg = 30°C (second heat) by DSC @10°C/min under N₂
 35 10% weight loss temperature 420°C @10°C/min under N₂
 Tm, none detected by DSC @10°C/min, N₂, second heat
 0.5 mole % perfluorocyclobutene by ¹⁹F NMR in melt at 320°C
 40.9 mole % HFP by ¹⁹F NMR in melt at 320°C
 58.6 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 3.8 kg/L/hr (31 lbs/gal/hr)

EXAMPLE 107

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/Perfluorocyclopentene

5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 137 g TFE, 20 g perfluorocyclopentene, and ~0.6 g of NF₃ was made in 96.5 MPa reservoir (2). About 1578 g of this mixture were run through the 10 ml shaken autoclave at 350°C and 96.5 MPa over a 110 minute period. Drying the product under vacuum and then for four hours at 150°C under vacuum gave 217.1 g of
10 white polymer.

1 g/5 FC-75 at r.t., clear to hazy, trace flocculent solid

Mw = 103,000 by GPC in FC-75 at 80°C

Mn = 30,600 by GPC in FC-75 at 80°C

Melt index_{120°C}, 5 kg = 1 g/min

15 Tg = 29°C (second heat) by DSC @10°C/min under N₂

10% weight loss temperature, 380°C, @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

0.6 mole % perfluorocyclopentene by ¹⁹F NMR in melt at 320°C

49.0 mole % HFP by ¹⁹F NMR in melt at 320°C

20 50.4 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 12 kg/L/hr (98 lbs/gal/hr)

EXAMPLE 108

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/Vinyl fluoride

25 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 111 g TFE, 10 g vinyl fluoride, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1663 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 135 minute period. Drying the product for 4 hours under vacuum at 150°C gave 91.6 g of colorless polymer.

30 1 g/5 ml CF₃CFHCFHCF₂CF₃ at r.t., hazy solution

Mw = 31,600 by GPC in FC-75 at 80°C (partial solubility)

Mn = 12,800 by GPC in FC-75 at 80°C (partial solubility)

Tg = 9°C (second heat) by DSC @10°C/min under N₂

10% weight loss temperature 370°C @10°C/min under N₂

35 Tm, none detected by DSC @10°C/min, N₂, second heat

16 mole % vinyl fluoride by ¹⁹F NMR in melt at 320°C

40 mole % HFP by ¹⁹F NMR in melt at 320°C

44 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 4.1 kg/L/hr (34 lbs/gal/hr)

EXAMPLE 109

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CF₂=C(CF₃)(C=O)F

- 5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 115 g TFE, 10 g CF₂=C(CF₃)(C=O)F, and ~0.6 g of NF₃ was made in 96.5 MPa reservoir (2). About 1411 g of this mixture were run through the 10 ml shaken autoclave at 300°C and 96.5 MPa over a 125 minute period. Drying the product for 4 hours under vacuum at 150°C gave 152 g of pale yellow polymer.
- 10 1 g/5 ml FC-75 at r.t., soluble, trace flocculent solids
 Mw = 138,000 by GPC in FC-75 at 80°C
 Mn = 50,000 by GPC in FC-75 at 80°C
 Melt index_{120°C, 5 kg} = 0.7 g/min
 Tg = 36°C (second heat) by DSC @10°C/min under N₂
 15 10% weight loss temperature 390°C @10°C/min under N₂
 Tm, none detected by DSC @10°C/min under N₂
 ~0.1 mole % CF₂=C(CF₃)COF by ¹⁹F NMR in melt at 320°C
 48.2 mole % HFP by ¹⁹F NMR in melt at 320°C
 51.7 mole % TFE by ¹⁹F NMR in melt at 320°C
 20 Productivity 7.3 kg/L/hr (61 lbs/gal/hr)

EXAMPLE 110

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CF₂=CFH

- 25 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 111 g TFE, 10 g CF₂=CFH, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1622 g of this mixture were run through the 10 ml shaken autoclave at 250°C and 96.5 MPa over a 150 minute period. Drying the product for 4 hours under vacuum at 150°C gave 109.8 g of colorless polymer.
- 30 1 g/5 ml FC-75 at r.t., clear solution, trace (?) insolubles
 Mw = 185,000 by GPC in FC-75 at 80°C
 Mn = 71,400 by GPC in FC-75 at 80°C
 Melt index_{120°C, 5 kg} = 0.3 g/min
 Tg = 27°C (second heat) by DSC @10°C/min under N₂
 10% wt. loss temperature, 420°C @10°C/min under N₂
 35 Tm, none detected by DSC @10°C/min. N₂, second heat
 7.8 mole % CF₂=CFH by ¹⁹F NMR in melt at 320°C
 39.2 mole % HFP by ¹⁹F NMR in melt at 320°C
 53.0 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 4.4 kg/L/hr (36 lbs/gal/hr)

EXAMPLE 111

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/Perfluoro-2-methylene-4-methyl-1,3-dioxolane

5 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 116 g TFE, 20 g perfluoro-2-methylene-4-methyl-1,3-dioxolane, and ~0.6 g of NF₃ was made in 96.5 MPa reservoir (2). About 1471 g of this mixture were run through the 10 ml shaken autoclave at 300°C and 96.5 MPa over a 140 minute period. Drying the product for 4 hours under vacuum at 150°C gave 156 g of
10 colorless polymer.

1 g/5 ml FC-75 at r.t., hazy solution, flocculent residue

Mw = 108,000 by GPC in FC-75 at 80°C

Mn = 39,400 by GPC in FC-75 at 80°C

Melt index_{120°C, 5 kg} = 1.1 g/min

15 Tg = 31°C (second heat) by DSC @10°C/min under N₂

10% wt. loss temperature, 370°C @ 10°C/min under N₂

Tm, none detected by DSC @10°C/min under N₂

2.3 mole % perfluoro-2-methylene-4-methyl-1,3 dioxolane by ¹⁹F

NMR in melt at 320°C

20 46.0 mole % HFP by ¹⁹F NMR in melt at 300°C

51.7 mole % TFE by ¹⁹F NMR in melt at 300°C

Productivity 6.7 kg/L/hr (56 lbs/gal/hr)

EXAMPLE 112

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/VF₂

25 The same set up was used as in Example 1. A mixture of 4000 g of HFP, 100 g TFE, 100 g vinylidene fluoride, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 3771 g of this mixture were run through the 10 ml shaken autoclave at 225°C and 96.5 MPa over a 325 minute period. Drying the product
30 first under vacuum and then for 4 hours at 150°C gave 225 g of white polymer. Analysis results are shown below.

1 g/5 ml of CF₃CFHCFHCF₂CF₃, clear solution at room temperature

Mw = 318,000 by GPC in FC-75 at 80°C

Mn = 100,000 by GPC in FC-75 at 80°C

35 Melt index_{160°C, 15 kg} = 0.3 g/min

Tg = 2°C (second heat) by DSC @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

10% weight loss temperature 420°C by TGA @10°C/min under N₂

~36 mole % VF2*

~44 mole % HFP*

~20 mole % TFE*

Productivity 4.2 kg/L/hr (35 lbs/gal/hr)

- 5 * Combined ^{19}F NMR results in melt at 320°C with ^1H and ^{19}F NMR results obtained after 1,4-dichloro-2-trifluoromethylbenzene has added as a gravimetric internal standard and the sample dissolved as well as possible in room temperature hexafluorobenzene.

EXAMPLE 113

10 Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/VF2

- The same set up was used as in Example 1. A mixture of 4000 g of HFP, 200 g TFE, 5 g vinylidene fluoride, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 3932 g of this mixture were run through the 10 ml shaken
15 autoclave at 225°C and 96.5 MPa over a 380 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 116 g of white polymer. Analysis results are shown below.

1 g/5 ml FC-75, clear, viscous solution at r.t.

Mw = 428,000 by GPC in FC-75 at 80°C

- 20 Mn = 181,000 by GPC in FC-75 at 80°C

Melt index_{260°C, 15 kg} = 0.8 g/min

Tg = 19°C (second heat) by DSC @10°C/min under N_2

Tm, none detected by DSC @10°C/min, N_2 , second heat

10% weight loss temperature 420°C by TGA @10°C/min under N_2

- 25 ~10 mole % VF2*

~34 mole % HFP*

~56 mole % TFE*

Productivity 1.8 kg/L/hr (15 lbs/gal/hr)

- 30 * Combine ^{19}F NMR results in melt at 320°C with ^1H and ^{19}F NMR results obtained after 1,4-dichloro-2-trifluoromethylbenzene has added as a gravimetric internal standard and the sample dissolved as well as possible in room temperature hexafluorobenzene.

EXAMPLE 114

Continuous Polymerization in 10 ml Autoclave with Agitation

- 35 HFP/VF2

A. At 225°C: The same set up was used as in Example 1. A mixture of 2000 g of HFP, 80 g vinylidene fluoride, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1600 g of this mixture were run through the 10 ml shaken

autoclave at 225°C and 96.5 MPa over a 135 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 82 g of white polymer.

Analysis results are shown below.

- 1 g/5 ml $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ at r.t., clear, highly viscous
 5 Inherent Viscosity in $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ at 25°C = 0.578
 $T_g = 2^\circ\text{C}$ (second heat) by DSC @10°C/min under N_2
 T_m , none detected by DSC @10°C/min, N_2 , second heat
 10% weight loss temperature 430°C by TGA @10°C/min under N_2
 ~53 mole % VF2 by ^{19}F NMR in melt at 300°C
 10 ~47 mole % HFP by ^{19}F NMR in melt at 300°C
 Productivity 3.6 kg/L/hr (30 lbs/gal/hr)

- B. At 200°C: The same set up was used as in Example 1. A mixture of 2000 g of HFP, 80 g vinylidene fluoride, and ~1.2 g of NF_3 was made in 96.5 MPa reservoir (2). About 1681 g of this mixture were run through the 10 ml shaken
 15 autoclave at 200°C and 96.5 MPa over a 110 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 38 g of white polymer.
 Analysis results are shown below.

- 1 g/5 ml $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ at r.t., clear, highly viscous
 Inherent Viscosity in $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ at 25°C = 0.793
 20 $T_g = 0^\circ\text{C}$ (second heat) by DSC @10°C/min under N_2
 T_m , none detected by DSC by TGA @10°C/min, N_2 , second heat
 10% weight loss temperature 430°C @10°C/min under N_2
 ~55 mole % VF2 by ^{19}F NMR in melt at 300°C
 ~45 mole % HFP by ^{19}F NMR in melt at 300°C
 25 Productivity 2.1 kg/L/hr (17 lbs/gal/hr)

EXAMPLE 115

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/ $\text{CH}_2=\text{CHO}(\text{C}=\text{O})\text{CF}_3$

- A. 225°C: The same set up was used as in Example 1. A mixture of
 30 4000 g of HFP, 220 g TFE, 5 g vinyl trifluoroacetate, and ~2.3 g of NF_3 was made in 96.5 MPa reservoir (2). About 4046 g of this mixture were run through the 10 ml shaken autoclave at 225°C and 96.5 MPa over a 300 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 147 g of white polymer. Analysis results are shown below.

- 35 1 g/5 ml FC-75, soluble with trace of flocculent solid
 $M_w = 151,000$ by GPC in FC-75 at 80°C
 $M_n = 49,500$ by GPC in FC-75 at 80°C
 Melt index_{160°C, 5 kg} = 4 g/min

Tg = 14°C (second heat) by DSC @10°C/min under N₂
 Tm, none detected by DSC @10°C/min, N₂, second heat
 10% weight loss temperature 380°C by DSC @10°C/min under N₂
 ~3.0 mole % CH₂=CHO(C=O)CF₃ by ¹⁹F NMR in melt at 340°C
 ~34.1 mole % HFP by ¹⁹F NMR in melt at 340°C
 ~62.9 mole % TFE by ¹⁹F NMR in melt at 340°C
 Productivity 2.9 kg/L/hr (24 lbs/gal/hr)

B. 200°C: The same set up was used as in Example 1. A mixture of
 4200 g of HFP, 220 g TFE, 5 g vinyl trifluoroacetate, and ~2.3 g of NF₃ was made
 in 96.5 MPa reservoir (2). About 4109 g of this mixture was run through the
 10 ml shaken autoclave at 200°C and 96.5 MPa over a 390 minute period. Drying
 the product first under vacuum and then for 4 hours at 150°C gave 84 g of white
 polymer. Analysis results are shown below.

1 g/5 ml FC-75, soluble with trace of flocculent solid
 Mw = 214,000 by GPC in FC-75 at 80°C
 Mn = 65,900 by GPC in FC-75 at 80°C
 Melt index_{160°C, 5 kg} = 1.3 g/min
 Tg = 24°C (second heat) by DSC @10°C/min under N₂
 Tm, none detected by DSC @10°C/min, N₂, second heat
 10% weight loss temperature 400°C by DSC @10°C/min under N₂
 ~4.3 mole % CH₂=CHO(C=O)CF₃ by ¹⁹F NMR in melt at 320°C
 ~31.0 mole % HFP by ¹⁹F NMR in melt at 320°C
 ~64.7 mole % TFE by ¹⁹F NMR in melt at 320°C
 Productivity 1.3 kg/L/hr (11 lbs/gal/hr)

EXAMPLE 116

Continuous Polymerization in 10 ml Autoclave with Agitation

HFP/TFE/CFH=CF₂

The same set up was used as in Example 1. A mixture of 2000 g of HFP,
 110 g TFE, 20 g trifluoroethylene, and ~1.2 g of NF₃ was made in 96.5 MPa
 reservoir (2). About 1694 g of this mixture was run through the 10 ml shaken
 autoclave at 200°C and 96.5 MPa over a 145 minute period. Drying the product
 first under vacuum and then for 4 hours at 150°C gave 54 g of white polymer.
 Analysis results are gathered below.

1 g/10 ml FC-75, very viscous, incomplete solution
 Mw = 613,000 by GPC in FC-75 at 80°C
 Mn = 137,000 by GPC in FC-75 at 80°C
 Melt index_{160°C, 15 kg} = 0.7 g/min
 Tg = 25°C (second heat) by DSC @10°C/min under N₂

T_m, none detected by DSC @10°C/min, N₂, second heat
 10% weight loss temperature 420°C by DSC @10°C/min under N₂
 ~20.0 mole % CHF=CF₂ by ¹⁹F NMR in melt at 250°C
 ~28.1 mole % HFP by ¹⁹F NMR in melt at 250°C
 ~51.9 mole % TFE by ¹⁹F NMR in melt at 250°C
 Productivity 2.2 kg/L/hr (19 lbs/gal/hr)

EXAMPLE 117**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/CH₂=CHF**

10 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, 20 g vinyl fluoride, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2). About 1752 g of this mixture was run through the 10 ml shaken autoclave at 200°C and 96.5 MPa over a 135 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 59 g of white polymer. Analysis
 15 results are gathered below.

1 g/5 ml CF₃CFHCFHCF₂CF₃ highly viscous, hazy solution

Melt index_{160°C, 15 kg} = 0.5 g/min

T_g = 10°C (second heat) by DSC @10°C/min under N₂

T_m, none detected by DSC @10°C/min, N₂, second heat

20 10% weight loss temperature 420°C by DSC @10°C/min under N₂
 ~34.1 mole % CH₂=CHF by ¹⁹F NMR in melt at 300°C
 ~31.9 mole % HFP by ¹⁹F NMR in melt at 300°C
 ~34.0 mole % TFE by ¹⁹F NMR in melt at 300°C
 Productivity 2.6 kg/L/hr (22 lbs/gal/hr)

EXAMPLE 118**Continuous Polymerization in 10 ml Autoclave with Agitation****HFP/TFE/FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ (PSEPVE)**

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, 50 g PSEPVE, and ~1.2 g of NF₃ was made in 96.5 MPa reservoir (2).
 30 About 1857 g of this mixture was run through the 10 ml shaken autoclave at 200°C and 96.5 MPa over a 165 minute period. The initial product was a thick fluid. Drying the product first under vacuum and then for 4 hours at 150°C gave 21 g of polymer. Analysis results are shown below.

1 g/5 ml of FC-75, partial solution at room temperature

35 M_w = 97,700 by GPC in FC-75 at 80°C

M_n = 20,200 by GPC in FC-75 at 80°C

T_g = 17°C (second heat) by DSC @10°C/min under N₂

T_m, none detected by DSC @10°C/min, N₂, second heat

¹⁹F NMR in Hexafluorobenzene solution at 80°C

~1.4 mole % PSEPVE as free monomer

~1.4 mole % PSEPVE terpolymerized

~27.6 mole % HFP terpolymerized

5 ~69.6 mole % TFE terpolymerized

Productivity 0.8 kg/L/hr (6.5 lbs/gal/hr)

EXAMPLE 119

Continuous Polymerization in 10 ml Autoclave with Agitation

CF₃CF₂CF₂CF₂N=NCF₂CF₂CF₂CF₃ Initiation

10 The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 0.7 g of CF₃CF₂CF₂CF₂N=NCF₂CF₂CF₂CF₃ dissolved in 2 ml HFP cyclic dimer (perfluorodimethylcyclobutane) was made in 96.5 MPa reservoir (2). About 1760 g of this mixture was run through the 10 ml shaken autoclave at 350°C and 96.5 MPa over a 145 minute period. Drying the product first under
15 vacuum and then for 4 hours at 150°C gave 120 g of white polymer. Analysis results are shown below.

1 g/5 ml of FC-75, clear solution, trace flocculent solid

Mw = 174,000 by GPC in FC-75 at 80°C

Mn = 62,200 by GPC in FC-75 at 80°C

20 Melt index_{160°C, 5 kg} = 0.9 g/min

Tg = 31°C (second heat) by DSC @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

10% weight loss temperature 400°C by DSC @10°C/min under N₂

~47 mole % HFP by ¹⁹F NMR in melt at 320°C

25 ~53 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 5.0 kg/L/hr (41 lbs/gal/hr)

EXAMPLE 120

Continuous Polymerization in 10 ml Autoclave with Agitation

CF₃CF₂CF₂OCF(CF₃)SO₂(CF₂)₇CF₃ Initiation

30 A. 65.5 MPa: The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 2.5 g of CF₃CF₂CF₂OCF(CF₃)SO₂(CF₂)₇CF₃ dissolved in 2 ml HFP cyclic dimer (perfluorodimethylcyclobutane) was made in 96.5 MPa reservoir (2). About 1674 g of this mixture was run through the 10 ml shaken autoclave at 350°C and 62.3 to 70.5 MPa (~65.5 MPa average) over a
35 110 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 120 g of white polymer. Analysis results are shown below.

1 g/5 ml of FC-75, partial solubility at room temperature

Mw = 125,000 by GPC in FC-75 at 80°C

Mn = 56,600 by GPC in FC-75 at 80°C

Melt index_{160°C, 5 kg} = 1.6 g/min

Tg = 27°C (second heat) by DSC @ 10°C/min under N₂

Tm, none detected by DSC @ 10°C/min, N₂, second heat

5 10% weight loss temperature 420°C by DSC @ 10°C/min under N₂

~44 mole % HFP by ¹⁹F NMR in melt at 320°C

~56 mole % TFE by ¹⁹F NMR in melt at 320°C

Productivity 6.5 kg/L/hr (54 lbs/gal/hr)

B. 96.5 MPa: The same set up was used as in Example 1. A mixture of
 10 2000 g of HFP, 110 g TFE, and 2.5 g of CF₃CF₂CF₂OCF(CF₃)SO₂(CF₂)₇CF₃
 dissolved in 2 ml HFP cyclic dimer (perfluorodimethylcyclobutane) was made in
 3.8 L reservoir (2). About 1552 g of this mixture was run through the 10 ml
 shaken autoclave at 350°C and 96.5 MPa over a 140 minute period. Drying the
 product first under vacuum and then for 4 hours at 150°C gave 148 g of white
 15 polymer. Analysis results are shown below.

1 g/5 ml of FC-75, clear solution, trace flocculent solid

Mw = 115,000 by GPC in FC-75 at 80°C

Mn = 53,400 by GPC in FC-75 at 80°C

Melt index_{160°C, 5 kg} = 2.7 g/min

20 Tg = 29°C (second heat) by DSC @ 10°C/min under N₂

Tm, none detected by DSC @ 10°C/min, N₂, second heat

10% weight loss temperature 410°C by DSC @ 10°C/min under N₂

42 mole % HFP by ¹⁹F NMR in melt at 300°C

58 mole % TFE by ¹⁹F NMR in melt at 300°C

25 Productivity 6.3 kg/L/hr (53 lbs/gal/hr)

EXAMPLE 121

Preparation of Perfluoro-1-propoxyethyl octyl sulfone



A solution of perfluoro-1-propoxyethanesulfonyl fluoride (18.6 g,
 30 50.4 mmol, perfluoro-1-propoxyethanesulfonyl fluoride was prepared by the
 method of S. Temple, *J. Org. Chem.* 1968, 33, 344) and perfluorooctyl-
 trimethylsilane (11.8 g, 24 mmol, perfluorooctyltrimethylsilane was prepared as
 described in U. S. Patent 5,171,893) in trifluorotoluene (24 mL) was cooled to
 ca. -11°C and treated with tris(piperidino)sulfonium benzoate (144 mg,
 35 0.35 mmol). The reaction was allowed to warm slowly to 25°C. After 0.5 hr,
 another 144 mg of tris(piperidino)sulfonium benzoate was added, resulting in
 additional color and a mild exotherm. After stirring for 18 hr., volatile components
 were transferred from the vessel under vacuum, collecting solvent first, then higher

boiling material which was redistilled to afford 6.8 g (37%) of product with bp = 45-47°C/0.05 mm Hg which was homogeneous by gas chromatographic analysis. ^{19}F NMR (THF- d_8): -77.2 (m), -80.7 (m), -81.3 (t, J = 10 Hz), -81.67 (t, J = 7.3 Hz), -104.4 and -105.4 (AB pattern, J = 246 Hz), singlets at -119.5, -121.4, -121.7, -121.95, -122.8, -123.8, -126.3, and -129.4, in accord with the desired structure, $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{SO}_2(\text{CF}_2)_7\text{CF}_3$.

EXAMPLE 122

Continuous Polymerization in 10 ml Autoclave with Agitation

$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{SO}_2\text{F}$ Initiation

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 1.2 g of $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{SO}_2\text{F}$ dissolved in 2 ml HFP cyclic dimer (perfluorodimethylcyclobutane) was made in 3.8 L reservoir (2). About 1604 g of this mixture was run through the 10 ml shaken autoclave at 350°C and 96.5 MPa over a 135 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 80 g of white polymer. Analysis results are shown below.

1 g/5 ml of FC-75, clear solution at room temperature
 Mw = 343,000 by GPC in FC-75 at 80°C
 Mn = 106,000 by GPC in FC-75 at 80°C
 Melt index_{160°C, 15 kg} = 0.3 g/min
 Tg = 32°C (second heat) by DSC @10°C/min under N_2
 Tm, none detected by DSC @10°C/min, N_2 , second heat
 10% weight loss temperature 420°C by DSC @10°C/min under N_2
 ~45 mole % HFP by ^{19}F NMR in melt at 320°C
 ~55 mole % TFE by ^{19}F NMR in melt at 320°C
 Productivity 3.6 kg/L/hr (30 lbs/gal/hr)

EXAMPLE 123

Continuous Polymerization in 10 ml Autoclave with Agitation

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{Cl}$ Initiation

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 1 g of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{Cl}$ dissolved in 2 ml HFP cyclic dimer (perfluorodimethylcyclobutane) was made in reservoir (2). About 1585 g of this mixture was run through the 10 ml shaken autoclave at 350°C and 14,000 over a 140 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 94 g of perhaps slightly gray polymer. Analysis results are shown below.

1 g/5 ml of FC-75, clear solution with trace of flocculent solid
 Mw = 276,000 by GPC in FC-75 at 80°C

Mn = 76,100 by GPC in FC-75 at 80°C

Melt index_{160°C, 15 kg} = 0.9 g/min

Tg = 31°C (second heat) by DSC @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

5 10% weight loss temperature 410°C by DSC @10°C/min under N₂

46 mole % HFP by ¹⁹F NMR in melt at 300°C

54 mole % TFE by ¹⁹F NMR in melt at 300°C

Productivity 4.0 kg/L/hr (33 lbs/gal/hr)

EXAMPLE 124

10 Continuous Polymerization in 10 ml Autoclave with Agitation

ClSO₂Cl Initiation

The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 1 g of ClSO₂Cl dissolved in 2 ml HFP cyclic dimer (perfluoro-dimethylcyclobutane) was made in reservoir (2). About 1620 g of this mixture was
15 run through the 10 ml shaken autoclave at 300°C and 96.5 MPa over a 155 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 63 g of polymer. Analysis results are shown below.

1 g/5 ml of FC-75, clear solution at room temperature

Mw = 319,000 by GPC in FC-75 at 80°C

20 Mn = 111,000 by GPC in FC-75 at 80°C

Melt index_{160°C, 15 kg} = 1.3 g/min

Tg = 32°C (second heat) by DSC @10°C/min under N₂

Tm, none detected by DSC @10°C/min, N₂, second heat

10% weight loss temperature 410°C by DSC @10°C/min under N₂

25 42 mole % HFP by ¹⁹F NMR in melt at 300°C

58 mole % TFE by ¹⁹F NMR in melt at 300°C

Productivity 2.4 kg/L/hr (20 lbs/gal/hr)

EXAMPLE 125

Continuous Polymerization in 10 ml Autoclave with Agitation

30 HFP/TFE/CH₂=CHCH₂Si(OMe)₃

The same set up was used as in Example 1. A mixture of 4000 g of HFP, 220 g TFE, 4 ml of allyltrimethoxysilane, and ~2.3 g of NF₃ was made in reservoir (2). About 3919 g of this mixture was run through the 10 ml shaken autoclave at 225°C and 96.5 MPa over a 330 minute period. Drying the product under vacuum
35 at room temperature gave 99 g of white polymer. A melt index at 100°C with a 5 kg weight gave a flow of 1.6 g/min, but after exposing 8 g of polymer to 25 ml water + 1 ml CF₃COOH first at r.t. and then at reflux, a temperature of 160°C was needed to obtain comparable flow rates, 2 g/min with a 5 kg weight. Composition

was determined by ^{19}F NMR on the polymer melt at 320°C , using the $\text{CF}(\text{CF}_3)\text{CH}_2$ peak at 77 ppm to estimate a minimum allyltrimethoxysilane content. Fluorine NMR also found peaks for $-\text{CFH}-$ groups at 208-212 ppm, which if calculated as a monomer unit, would make up 2.2 mole % (0.61 wt %) of the polymer. Analytical results are shown below.

- 5 1 g/5 ml of FC-75, partial, hazy solution at room temperature
 Mw = 51,800 by GPC in FC-75 at 80°C
 Mn = 14,900 by GPC in FC-75 at 80°C
 Melt index $_{100^\circ\text{C}, 5 \text{ kg}} = 1.6 \text{ g/min}$
 10 Tg = 10°C (second heat) by DSC @ 10°C/min under N_2
 Tm, none detected by DSC @ 10°C/min , N_2 , second heat
 ≥ -4.2 mole % allyltrimethoxysilane by ^{19}F NMR in melt at 320°C^*
 ≤ 32.6 mole % HFP by ^{19}F NMR in melt at 320°C
 ≤ 61.0 mole % TFE by ^{19}F NMR in melt at 320°C
 15 ≤ 2.2 mole % $-\text{CFH}-$ by ^{19}F NMR in melt at 320°C
 Productivity 1.8 kg/L/hr (15 lbs/gal/hr)
 * Assumes that the $-\text{CF}(\text{CF}_3)\text{CH}_2-$ sequence at -77 ppm accounts for all incorporated allyltrimethoxysilane.

EXAMPLE 126

20 Continuous Polymerization in 10 ml Autoclave with Agitation HFP/TFE/ $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OCH}(\text{CF}_3)_2$

- The same set up was used as in Example 1. A mixture of 2000 g of HFP, 110 g TFE, and 5 g of 1,1,1,3,3,3-hexafluoroisopropyl acrylate was made in reservoir (2). About 1276 g of this mixture was run through the 10 ml shaken
 25 autoclave at 250°C and 96.5 MPa over a 140 minute period. Drying the product first under vacuum and then for 4 hours at 150°C gave 85.9 g of polymer. Analysis results are shown below.

- 1 g/5 ml FC-75, soluble with trace of flocculent residue at r.t.
 Mw = 84,700 by GPC in FC-75 at 80°C
 30 Mn = 27,600 by GPC in FC-75 at 80°C
 Tg = 27°C (second heat) by DSC @ 10°C/min under N_2
 Tm, none detected by DSC @ 10°C/min , N_2 , second heat
 10% weight loss temperature 390°C by TGA @ 10°C/min under N_2
 ~ 3.2 mole % $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OCH}(\text{CF}_3)_2$ by ^{19}F NMR in melt at 250°C^*
 35 ~ 39.9 mole % HFP by ^{19}F NMR in melt at 250°C
 ~ 56.9 mole % TFE by ^{19}F NMR in melt at 250°C
 Productivity 3.6 kg/L/hr (31 lbs/gal/hr)

* Calculated from the excess integration of the $-CF_3$ resonances from -60 to -84 ppm over what would be expected from HFP's $-CF$ resonances from -175 to -186 ppm.

EXAMPLE 127

5 Perfluorosulfur Compounds as Solvents for Amorphous Fluoropolymers

A. Perfluoro-1,4-dithiane: A 0.1009 g sample of 44:56 poly(HFP:TFE), $M_w = 156,000$, was rolled in a vial with 1 ml (1.64 g) of perfluoro-1,4-dithiane for 2 hours at room temperature giving a solution.

10 B. Perfluorothiepane: A 0.2305 g sample of 42:58 poly(HFP:TFE), $M_w = 74,000$, was rolled in a vial with 1 ml (1.78 g) of perfluorothiepane for 24 hours at room temperature giving a viscous solution.

C. Perfluorodiethylsulfone: A 0.1 g sample of 45:55 poly(HFP:TFE), $M_w = 325,000$, was rolled in a vial with 1 ml of perfluorodiethylsulfone for 24 hours at room temperature giving a viscous solution.

15 D. Perfluorooctanesulfonyl fluoride: A 0.5 g sample of 46:54 poly(HFP:TFE), $M_w = 392,000$, was rolled in a vial with 5 ml of perfluorooctanesulfonyl fluoride giving a clear solution at room temperature. Another 0.5 g of polymer was added, going again into solution, but now very viscous.

EXAMPLE 128

20 The Use of Mixed Solvents

A. FC-75 and HFC's: A 1 g sample of 44:56 poly(HFP/TFE), $M_w = 285,000$ was dissolved in 5 ml of FC-75. About 6 to 7 ml of $CF_3CFHCFHCF_2CF_3$ had to be added with stirring before there was any sign of persistent haze or precipitate.

25 A 1 g sample of 45:55 poly(HFP/TFE), $M_w = 325,000$ was dissolved in 5 ml of FC-75. About 6 to 7 ml of $CF_3CF_2CF_2OCFHCF_3$ had to be added with stirring before there was any sign of persistent haze or precipitate.

30 B. Perfluorooctane and HCFC's: A 0.58 g sample of 45:55 poly(HFP/TFE), $M_w = 325,000$ was dissolved in 5 ml of perfluoroalkane (~perfluorooctane). About 6 to 8 ml of CF_3CHCl_2 had to be added with stirring before there was any sign of persistent haze or precipitate.

EXAMPLE 129

35 Aluminum coupons 2.5 cm X 7.6 cm X 0.64 mm were cleaned by washing with acetone and were dried for 1 h at 150°C. A solution of a 51 wt. % HFP/49 wt. % TFE copolymer (combined sample from Examples 1 to 13) was prepared by dissolving 1 g polymer in 99 g PF5080 solvent (3M Co., Minneapolis, MN, U.S.A., believed to be perfluorooctane). Two coats of solution were applied at room temperature to the surface of the cleaned aluminum coupons by spraying the

solution with an air brush at 207 kPa (absolute). The coatings were each dried and annealed for 4 h at 250°C in an air circulating oven.

One fluoropolymer coated coupon and one clean uncoated coupon were placed in a freezer at -17°C with three drops of water on each, one drop near each end and one drop in the center. After 4.75 h one drop near each end and one drop in the center. After 4.75 h the coupons were removed from the freezer and were immediately tested for adhesion of the frozen droplets to the metal by trying to peel the drops off of the surface with a thumb nail. The frozen droplets on the uncoated control were very difficult to remove. The frozen droplets on the fluoropolymer coated coupons fell off with very little force.

EXAMPLE 130

Aluminum cylinders 1.3 cm diameter X 7.6 cm length were cleaned by washing with acetone and were dried for 1 h at 150°C. The fluoropolymer solution used in Example 129 was used to coat one cylindrical surface. Two coats of solution were applied at room temperature to the surface of the cleaned aluminum cylinder by spraying the solution with an air brush at 207 kPa (absolute). The coatings were each dried and annealed for 4 h at 250°C in an air circulating oven.

One fluoropolymer coated cylinder and one clean uncoated cylinder were placed in a wind tunnel at -4°C and with air stream velocity of 67.1 m/sec. Droplets of water, 5 µm in diameter were sprayed into the air stream for 5.8 min. The supercooled droplets built up a horse shoe shaped ice formation, approximately 1.0 cm thick on both cylinders.

The ice coated cylinders were removed from the chamber. A flat scraper with an attached force gauge was used to immediately remove the ice from the cylinders. The force required to scrape the ice from the control, uncoated cylinder was 5.7 N. The force required to scrape the ice from the fluoropolymer coated cylinder was 0.64 N.

The cylinders were then placed back into the wind tunnel and the ice coating test repeated two more times. After the third exposure, the force required to scrape the ice from the control, uncoated cylinder was 6.2 N. The ice fell off the fluoropolymer coated as being removed from the chamber, with no applied scraping force.

EXAMPLE 131

Under the same testing protocol as for Example 130 above, a 40.6 mole % HFP/56.5 mole % TFE/2.9 mole % CTFE terpolymer (from Example 91) took 3.1 N and 4.1 N of force to scrape the ice from the test cylinder.

EXAMPLE 132

In this Example copolymers containing VF2 are analyzed for partial sequence distribution. Sequences are denoted by the Sequence No., as described above. Analyses were also done in solution as described above for these sequences.

The polymers analyzed are as follows. Polymer C is a VF2/HFP dipolymer prepared in Example 114A, while Polymer D is a VF2/HFP/TFE tripolymer prepared in Example 112. Viton[®] A and Viton[®] B fluoroelastomers are commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A., and are made by relatively (compared to the conditions for polymerizations herein) low temperature and low pressure free radical polymerization in aqueous emulsion.

In the Table below the compositions of these polymers are shown, together with partial sequence distributions.

Polymer	C	Viton [®] A	D	Viton [®] B
Composition, mole %				
VF2	53.5	78.0	36.0	61.0
HFP	46.5	22.0	44.0	17.0
TFE	-	-	20.0	22.0
Sequence No.	-----Mole Percent-----			
1+2	12.8	5.9	10.9	8.8
3+4	10.6	67.1	4.1	38.3
5	76.6	27.0	85.0	52.9

CLAIMS

What is claimed is:

1. A continuous polymerization process, comprising, contacting at a pressure of about 41 MPa to about 690 MPa, and a temperature of about 200°C to about 400°C, tetrafluoroethylene, hexafluoropropylene, and a radical initiator, to produce an amorphous polymer which contains at least 30 mole percent of repeat units derived from said hexafluoropropylene, at least 1 mole percent of repeat units derived from said tetrafluoroethylene, and provided that said continuous polymerization has an average residence time of about 5 seconds to about 30 minutes.
2. The process as recited in Claim 1 wherein said pressure is about 55 MPa to 172 MPa.
3. The process as recited in Claim 1 wherein said pressure is about 69 MPa to about 103 MPa.
4. The process as recited in Claim 1 wherein said temperature is about 225°C to about 400°C.
5. The process as recited in Claim 1 wherein said radical initiator is NF_3 , R_fNF , $\text{R}^1\text{N}=\text{NR}^1$, R_fOOR_f , R_fNF_2 , perfluoropiperazine, or a hindered perfluorocarbon of the formula $\text{C}_n\text{F}_{2n+2}$, hindered perfluoroalkenes of the formula C_nF_{2n} , a perfluoro(dialkylsulfone) of the formula $\text{R}^1\text{SO}_2\text{R}^1$, $\text{R}^1\text{SO}_2\text{F}$, $\text{R}^1\text{SO}_2\text{Cl}$, ClSO_2Cl , R^1I , IR^6I wherein the two iodides are not vicinal or geminal, perfluoro(dialkyldisulfides) R^1SSR^1 , perfluoro(trialkylamines) and perfluoroalkyl compounds containing nitrogen-sulfur bonds of the formula R^1_2NSR^1 , wherein each R_f is independently perfluoroalkyl, containing 1 to 20 carbon atoms, R^6 is perfluoroalkylene containing 3 to 20 carbon atoms, and each R^1 is independently saturated perfluorohydrocarbyl optionally containing one or more ether groups, isolated iodine, bromine or chlorine substituents, or perfluoroamino groups.
6. The process as recited in Claim 1 wherein said radical initiator is NF_3 , R_fNF , R_fNF_2 , perfluoropiperazine or a hindered perfluorocarbon of the formula $\text{C}_n\text{F}_{2n+2}$, wherein each R_f is independently perfluoroalkyl containing 1 to 20 carbon atoms.
7. The process as recited in Claim 1 wherein said average residence time is about 30 sec to about 5 min.
8. The process as recited in Claim 1 wherein another monomer which is an α -perfluoroolefin, a perfluorocycloolefin or a perfluoro(alkyl vinyl ether) is also present.
9. The process as recited in Claim 2 wherein said temperature is about 225°C to about 325°C, said radical initiator is NF_3 , and said average residence time is about 30 sec to about 5 min.

10. The process as recited in Claim 1 wherein said fluorinator is NF_3 .

11. An amorphous polymer, consisting essentially of, repeat units of the formula:

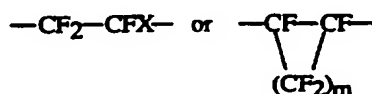
(a) at least about 30 mole percent of



(b) at least about 1 mole percent



(c) 0 to about 10 mole percent



(III)

wherein X is $-\text{C}_n\text{F}_{2n+1}$ or $-\text{OC}_n\text{F}_{2n+1}$, m is 2, 3 or 4, and n is an integer of 2 to 20, with $-\text{C}_n\text{F}_{2n+1}$ or an integer of 1 to 20 with $-\text{OC}_n\text{F}_{2n+1}$; and

provided that in said polymer less than 20 mole percent of (I) is present in the form of triads.

12. The polymer as recited in Claim 11 wherein (II) is at least about 30 mole percent of said repeat unit.

13. The polymer as recited in Claim 11 therein only (I) and (II) are present.

14. The polymer as recited in Claim 11 wherein (III) is about 0.1 to about 10 mole percent of said repeat units.

15. The polymer as recited in Claim 12 or 14 wherein (I) is about 50 to about 65 mole percent of said repeat units.

16. The polymer as recited in Claim 14 wherein X is $-\text{C}_n\text{F}_{2n+1}$, wherein n is 2 to 4.

17. The polymer as recited in Claim 14 wherein X is $-\text{OC}_n\text{F}_{2n+1}$, and n is an integer of 1 to 4.

18. The polymer as recited in Claim 11 or 12 wherein less than about 15 mole percent of (I) is present in the form of triads.

19. The polymer as recited in Claim 11 wherein less than about 10 mole percent of (I) is present in the form of triads.

20. A solution of the polymer of Claim 11.

21. The solution as recited in Claim 20 wherein a solvent is a perfluoro-carbon or a perfluoro compound containing sulfur, or a halogenated ether.

22. The polymer as recited in Claim 11 which has a molecular weight distribution of about 4 or less.

23. A fish hook coated with the polymer of Claim 11.

24. The process as recited in Claim 1 wherein said temperature is about 350°C to about 400°C, said initiator is a perfluorodialkylsulfone and the residence time is about 5 sec. to about 10 minutes.

25. The process of Claim 1 wherein the initiator is $C_2F_5SO_2C_2F_5$.

26. A continuous polymerization process, comprising, contacting at a pressure of about 41 MPa to about 690 MPa, and a temperature of about 200°C to about 400°C, tetrafluoroethylene, hexafluoropropylene, a third monomer and a radical initiator, to produce an amorphous polymer which contains at least 15 mole percent of repeat units derived from said hexafluoropropylene, at least 0-70 mole percent of repeat units derived from said tetrafluoroethylene, and 0-70 mole percent of repeat units derived from said third monomer, and provided that: said continuous polymerization has an average residence time of about 5 seconds to about 30 minutes; and said amorphous polymer contains at least one mole percent of repeat units derived from tetrafluoroethylene.

27. The process as recited in Claim 26 wherein said amorphous polymer contains at least 30 mole percent of repeat units derived from said hexafluoropropylene.

28. The process as recited in Claim 26 wherein said polymer contains:

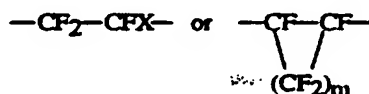
(a) at least about 30 mole percent of



(b) at least 1 mole percent



(c) 0 to about 10 mole percent



(III)

wherein X is $-C_nF_{2n+1}$ or $-OC_nF_{2n+1}$, m is 2, 3 or 4, and n is an integer of 2 to 20, with $-C_nF_{2n+1}$ or an integer of 1 to 20 with $-OC_nF_{2n+1}$; and

provided that in said polymer less than 20 mole percent of (I) is present in the form of triads.

29. The process of Claim 26 wherein said third monomer is vinylidene fluoride, provided that in said polymer less than 20 mole percent of the hexafluoropropylene is present in the form of triads.

30. The process of Claim 26 wherein the third monomer is present and is selected from the group consisting of: $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, ethylene, propylene, isobutylene, vinylidene fluoride, vinyl fluoride, trifluoroethylene, 4-bromo-3,3,4,4-tetrafluoro-1-butene, perfluoro(8-cyano-5-

- methyl-3,6-dioxo-1-octene), $\text{CF}_2=\text{CF}(\text{CF}_3)\text{COF}$, $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{R}^2$ wherein R^2 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CHR}^3$ wherein R^3 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OR}^4$ wherein R^4 is $\text{C}_n\text{F}_x\text{H}_y$ wherein $x+y = 2n+1$ and n is 1 to 8, allyltrimethoxysilane, perfluoro-cyclopentene, perfluorocyclobutene, $\text{CF}_2=\text{CFCF}_2\text{CN}$, $\text{CF}_2=\text{CFR}^5$ wherein R^5 is perfluoroalkyl optionally containing one or more of one or more ether groups, one cyano group, or one sulfonyl fluoride group, perfluoro(2-methylene-4-methyl-1,3-dioxolane), perfluoro(2-methyl-2,3-dihydro-1,4-dioxin), $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, methyl vinyl ether, $\text{CFCl}=\text{CF}_2$, $\text{CH}_2=\text{CFCF}_3$, $\text{CH}_2=\text{CHCF}_3$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFCF}_2\text{CN}$, and $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$.

31. The process as recited in Claim 30 wherein said third monomer is no more than 30 mole percent of repeat units in said amorphous polymer.
32. The process as recited in Claim 30 or 31 wherein no more than 20 mole percent of repeat units derived from hexafluoropropylene are present in a form of triads.
33. A compound of the formula $(\text{C}_4\text{F}_9)_2\text{NSCF}_3$.
34. A compound of the formula $\text{R}^6\text{R}^7\text{CFSO}_2\text{R}^8$, wherein R^6 is perfluoroalkyl, perfluoroalkyl containing one or more ether oxygen atoms, perfluoroalkoxy or perfluoroalkoxy containing one or more ether oxygen atoms, R^7 is perfluoroalkyl or perfluoroalkyl containing one or more ether oxygen atoms, and R^8 is perfluoroalkyl.
35. An amorphous polymer containing repeat units derived from:
 27-60 mole percent hexafluoropropylene, up to 35 mole percent total of one or more second monomers, and the balance tetrafluoroethylene, provided that at least one mole percent of TFE is present in the polymer, and wherein said second monomer is ethylene, vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene, 2,3,3,3-tetrafluoropropene, 4-bromo-3,3,4,4-tetrafluoro-1-butene, ethylene $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{R}^2$ wherein R^2 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CHR}^3$ wherein R^3 is perfluoro-n-alkyl containing 1 to 8 carbon atoms, $\text{CH}_2=\text{CH}(\text{C}=\text{O})\text{OR}^4$ wherein R^4 is $\text{C}_n\text{F}_x\text{H}_y$ wherein $x+y = 2n+1$ and n is 1 to 8, chlorotrifluoroethylene, or allyltrimethoxysilane;
 27-60 mole percent hexafluoropropylene, up to 5 mole percent total of one or more fourth monomers and the balance tetrafluoroethylene, provided that the polymer contains at least 1 mole percent tetrafluoroethylene, wherein said fourth monomer is perfluorocyclopentene, perfluorocyclobutene, $\text{CF}_2=\text{CFCF}_2\text{CN}$, $\text{CF}_2=\text{CFR}^5$ wherein R^5 is perfluoroalkyl optionally containing one or more of one or more ether groups, one cyano group, or one sulfonyl fluoride group.

perfluoro(2-methyl-4-methyl-1,3-dioxolane), perfluoro(2-methyl-2,3-dihydro-1,4-dioxin), or $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$; or

up to 30 mole percent total of one or more second monomers and up to 5 mole percent total of one or more fourth monomers.

5 36. The polymer as recited in Claim 35 wherein said second monomer is present and contains repeat units derived from 30-50 mole percent of hexafluoropropylene, and up to 20 mole percent of said second monomer.

37. The polymer as recited in Claim 35 wherein said second monomer is present and contains repeat units derived from 30-45 mole percent of hexafluoropropylene, and up to 10 mole percent of said second monomer.

38. The polymer as recited in Claim 35 wherein said fourth monomer is present and contains repeat units derived from 30-50 mole percent of hexafluoropropylene, and up to 2 mole percent of said second monomer.

39. The polymer as recited in Claim 35 wherein less than 20 mole percent of repeat units derived from hexafluoropropylene are present as triads.

40. An amorphous copolymer, consisting essentially of:

(a) >15 mole percent of the repeat unit



(b) at least 1 to about 60 mole percent of the repeat unit



(c) about 0.1 to about 85 mole percent of the repeat unit



wherein no more than about 20 mole percent of (I) is present in triads.

25 41. The copolymer as recited in Claim 40 wherein (I) is >30 mole percent of said repeat units, (II) is about 0.1 to about 65 mole percent of said repeat units.

42. An amorphous copolymer, consisting essentially of repeat units of the formula:

(a) >15 mole percent of the repeat unit



(c) about 0.1 to about 85 mole percent of the repeat unit



wherein no more than about 20 mole percent of (I) is present in triads.

35 43. The copolymer as recited in Claim 42 wherein (I) is >30 mole percent of said repeat units, and (IV) is about 0.1 to about 70 mole percent of said repeat units.

44. A film of the polymer of Claim 11, 35, 40 or 42.

45. A coating of the polymer of Claim 11, 35, 40 or 42.

46. An encapsulant of the polymer of Claim 11, 35, 40 or 42.
47. A solution of the polymer of Claim 11, 35, 40 or 42.
48. A fabric coated with the polymer of Claim 11, 35, 40 or 42.
49. An object coated or encapsulated with the polymer of Claim 11, 35, 40
5 or 42.
50. A mold release comprising the polymer of Claim 11 or 35.
51. A mold or extrusion die coated with the polymer of Claim 11 or 35.
52. A blend of a polyolefin and the polymer of Claim 11, 35, 40 or 42,
wherein the polymer of Claim 11, 35, 40 or 42 is about 50 to about 1,000 parts per
10 million by weight of the total of said polyolefin and said polymer of Claim 11, 35,
40 or 42.
53. The polymer as recited in Claim 11, 35, 40 or 42 which is crosslinked.
54. An ice release coating comprising the polymer of Claim 11, 40 or 42.
55. The compound as recited in Claim 34 wherein R⁸ is perfluoro-n-alkyl
15 containing 1 to 20 carbon atoms.
56. The compound as recited in Claim 34 wherein R⁶ is perfluoro-n-
propoxy, R⁷ is trifluoromethyl, and R⁸ is perfluoro-n-octyl.
57. The solution as recited in Claim 47 wherein a solvent is a mixed
solvent.

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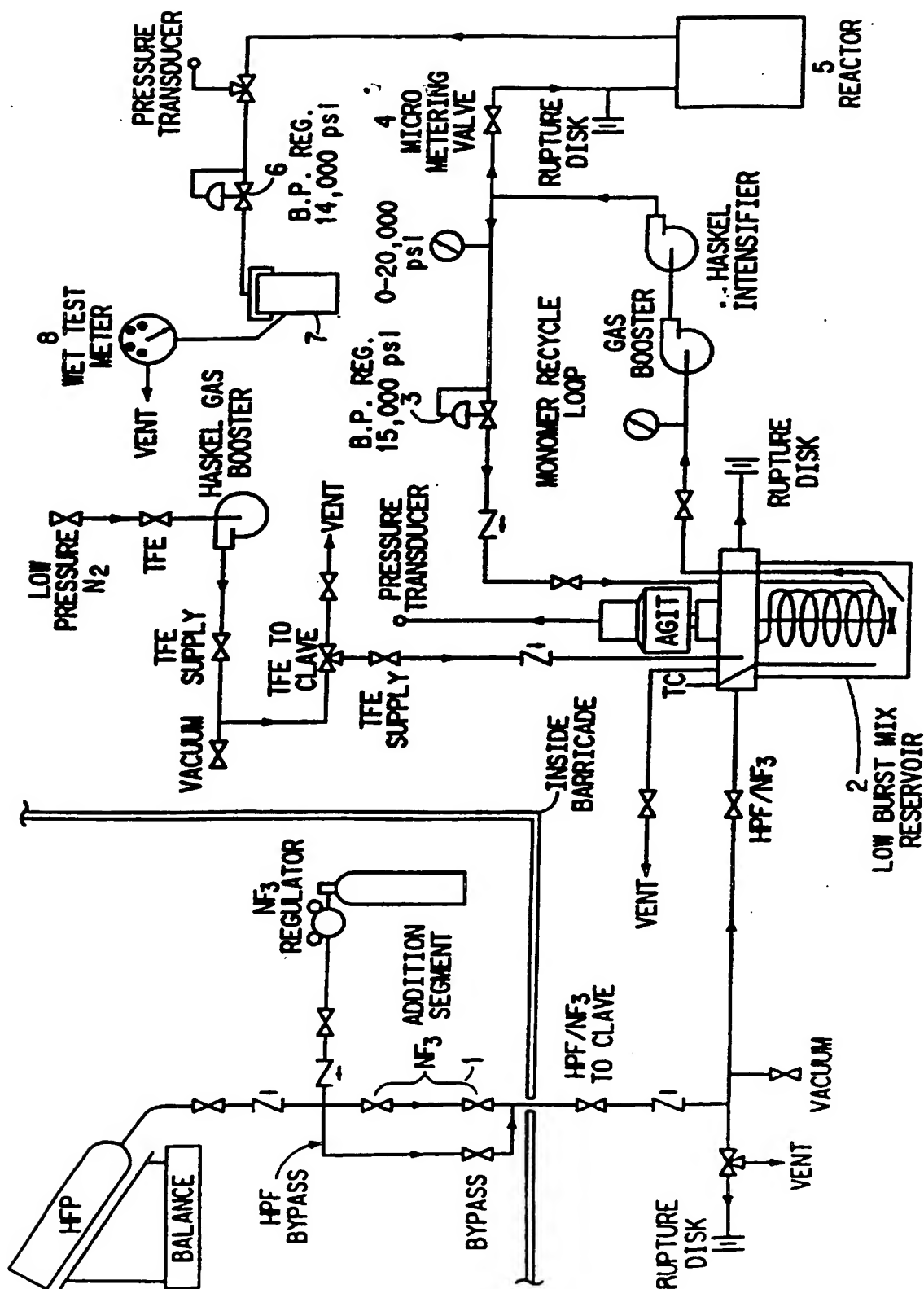


FIG. 1

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